# TOC Standard Development for Exploration-Class TOCA: 2024 Update

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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. 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. This paper explores the concept and practice of using a packed bed doser to generate a TOC standard solution for an online calibration method.**

## Acronyms and Nomenclature

| | | | | | |
|---|---|---|---|---|---|
| *DI* | = | deionized | *ECLSS* | = | Environmental Control and Life Support System |
| *IBA* | = | 4-iodobenzoic acid | *ISS* | = | International Space Station |
| *KSC* | = | Kennedy Space Center | *L* | = | liter |
| *LSS* | = | Life Support Systems | *MCO* | = | Mars Campaign Office |
| *min* | = | minute | *mL* | = | milliliter |
| *mm* | = | millimeter | *NASA* | = | National Aeronautics and Space Administration |
| *mol* | = | moles | *PBD* | = | packed bed doser |
| *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 |

## 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. 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. The ISS TOCA uses pre-packaged ground-supplied TOC calibration standards; however, solution stability becomes a concern when storing the standards beyond 18 months. MiniTOCA requires standards with a component shelf life longer than three years for exploration missions. In addition

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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 provides an update to the ongoing development of a calibration concept for an exploration-class TOC analyzer.[6]

## II. Background

Based on MiniTOCA operational requirements for the TOC calibration standard, the threshold target measurement range is 1 to 10 ppm TOC, with a goal range of 0.25 to 10 ppm TOC. The method detection limit, determined by the Environmental Protection Agency method, 40 CFR Part 136[7] is currently reported as 0.25 ppm. The measurement accuracy and precision are both required to be better than 25%, with a goal of precision better than 10%.[1] The MiniTOCA's sampling flow rate is controlled at 0.4mL/min; therefore, the TOC calibration standard should achieve a stable effluent TOC concentration in the target calibration range (0.25 to 10 ppm) at this flow rate. Lastly, the current pump in the MiniTOCA design limits the allowable pressure drop for any in-line TOC calibration standard, to preferably be no greater than 0.25 psi. These are the operational requirements for which the calibration technology concepts are being designed.

A preliminary trade study of concepts for providing on-orbit TOC calibration was conducted. Four concepts for calibration technologies were considered, as described in Table 1. The concepts are listed with their perceived advantages and disadvantages. A more detailed discussion on these various concepts have been previously reported.[6] Concept 1, using ground-filled standards, is the current state-of-the-art for on-orbit TOCA calibration. Concept 4, use of gas standards, was considered for its simplicity and accuracy, but was not selected as it does not provide a complete system calibration. Concept 2, implementing dilution of a liquid or solid concentrate, and Concept 3, a packed bed doser (PBD) were considered the best long-term solutions since these calibration methods promote stability through use of concentrates and by the *in situ*/real time addition of water to make standards on demand. Due to Kennedy Space Center (KSC)'s previous experience with developing like passive dosing technology, KSC was identified to develop Concept 3, the Packed Bed Doser.[8,9] As a calibration technology, Concept 3 was considered to be of a low Technology Readiness Level (TRL) and suitable for a dedicated feasibility study. The Concept 3 feasibility study is the focus of this paper.

**Table 1. Concepts Considered for TOC Calibration Standards.**

| Concept Number | Name | Explanation | Advantage | Disadvantage |
|---|---|---|---|---|
| 1 | Ground Filled Standards | Predetermined standards made on the ground | Existing technology for on-orbit TOCA calibration | Limited Stability Data (up to 18 months) |
| 2 | Dilution (or dissolution) | On-orbit TOC standard solution from a liquid concentrate or solid | Simple, stable, mass saving | Need low TOC water (not readily available) |
| 3 | Packed Bed Doser (PBD) | Pass water through a packed bed to create a standard solution by dissolution | Stable, mass saving, possible for automation | Need low TOC water, added system complexity, Low TRL |
| 4 | Gas Standard | Use compressed $CO_2$ to calibrate the detector system | Accurate for detector calibration, possible for automation | Calibration for the detector only, not for the whole system (TOC oxidation or $CO_2$ transport efficiencies) |

## III. Technical Approach: A Review

### A. Calibration Method Proposed

The detector response of the MiniTOCA instrument, like other TOC analyzers with a Non-Dispersive Infrared Detector (NDIR), can be linearly correlated to sample concentration. 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 that can be used as a calibration curve:

$$Y = mX + b$$

In this case, $Y$ is the area under the detector signal response (peak area under the curve), $X$ is the TOC concentration in water, $m$ is the slope of the linear regression line, and $b$ is the intercept.

While some nuances exist in the specific calibration method for the MiniTOCA instrument, a typical linear regression calibration requires high-purity water to be used as a blank standard and as the solvent to prepare TOC standard solutions. Thus, Concept 3 would need a source of low TOC water, which is not readily available in the spacecraft. A potential solution is to use a water purifier cartridge. However, such solutions increase the overall system complexity and mass. We have proposed an alternative calibration method to address the low TOC water challenge. Described previously, this method creates a calibration curve based on linear regression, but uses the standard addition method to obtain the slope ($m$) of the calibration curve and a recirculation method to obtain the system blank, or intercept ($b$).[6]

*1. Standard Addition Method for Obtaining the Slope*

Standard addition involves adding known amounts of analyte to an unknown sample, a process known as spiking. By increasing the number of the sample spikes, original unknown analyte concentration in the sample can be extrapolated from the calibration curve.[10] The standard addition method has been used for TOC analyzer calibration.[11] When this method is used, the standard is added directly to the aliquots of the analyzed sample. This method can 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:

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

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. [6]

*2. The Instrument Blank by the Recirculation Method as the Intercept [11]*

As mentioned above, the slope of the linear calibration curve $m$ can be obtained using the standard addition method, but not the intercept ($b$). Nonetheless, this could be "good enough" when the calibration curve's intercept is considered negligibly small. That is usually true 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 cannot be ignored for accurate measurements.

The positive signal representing the "blank" value 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, contamination of glassware, etc.)

While minimizing environmental contamination to an acceptable level is not trivial, it is possible through 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 recirculation 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.[6]

### B. Hardware Design Concept

Based on the MiniTOCA design requirements listed in the Background Section above, it was decided that the Concept 3 design should be developed following criteria in mind: (1) use of a packed bed filled with a solid TOC standard material with a constant surface area and a low solubility, (2) build from materials that do not leach TOC, such as stainless steel and glass. The constant area is essential to the dissolution rate, as described by the Noyes-Whitney equation. [12,13] To achieve a stable surface area, several slightly different designs were considered, Table 2. Among these potential design solutions, the packed bed with coated TOC beads was determined to provide the most stable TOC level in the effluent and was chosen for further development.[6]

**Table 2. Different Designs Considered for the Packed Bed Doser.**

| Potential Solution | Advantages | Disadvantages |
|---|---|---|
| Solute Particles in Foam Matrix | Existing technology at KSC | Foam is likely to leach TOC |
| Packed Bed with Solute Particles | No TOC leaching, long life span | Surface area is likely to change over time |
| Packed Bed with Coated Media Beads | No TOC leaching, constant surface area over the service life | Need to coat these beads! |

## IV. Earlier Work: Path Traveled and Lessons Learned (So Far)

### A. Path Traveled (So Far)

*1. The First PBD Prototype*

The first doser prototype was built with plastic and glass components, and the TOC levels were analyzed using an Anatel PAT 700 TOC analyzer (Beckman Coulter) with a conductivity sensor. This allowed development of test methods, measurement of pressure drop, and testing the effect of the flow rate on system performance. However, the plastic components were also found to leach unacceptable levels of TOC, so a second-generation stainless-steel cartridge was built for further testing.

**Figure 1. The first doser prototype: building material, test setup, and the TOC analyzer used for water analysis (shown from left to right).**

*2. The Second PBD Prototype*

The second prototype was built with a stainless-steel spool cartridge (~ 100 mL) with various connectors. The original components are shown in Figure 2. The rubber seal was identified as a TOC-leaching part and was replaced by a Teflon O-ring, which showed minimal TOC leaching over time.

The stainless-steel prototype was first tested with uncoated glass beads with the standard material (~ 20 grams). Those early tests revealed unexpected ion leaching into the passed water from the glass and ceramic media. The

leached ions interfered with the TOC analyzer PAT 700 conductivity-based detector system. The PAT 700 was replaced by a Shimadzu TOC-L instrument that uses a non-dispersive infrared detector (NDIR).

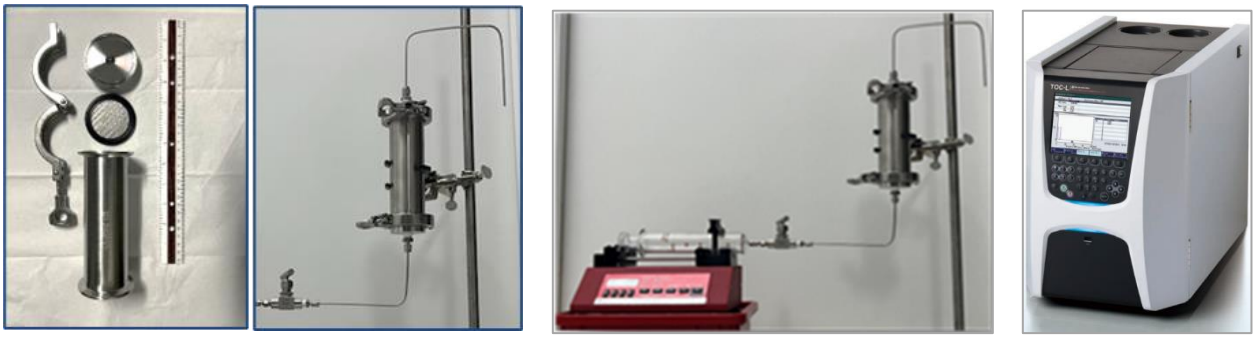


**Figure 2. The second doser prototype: building material, test setup, and the TOC analyzer used for water analysis (shown from left to right).**

Processes were developed to coat glass and ceramic beads with the first standard material selected, Irganox 1035, using a rotavapor. Up to 5% of the standard materials were coated on 0.3 to 1 mm glass and ceramic beads through a multi-step process. Figure 3 shows pictures of the 1 mm glass beads taken by a Keyence VHS digital microscope during the coating process.

Test was also carried out using coated ceramic beads and it revealed the long period of time needed to reach a steady state output of TOC. This issue was eventually attributed to the relatively low purity of the first standard material selected (Irganox 1035, TCI Chemicals, Lot 57ZNG, Certification Purity (HPLC area): 98%, Certificate of Analysis: 99.6%).

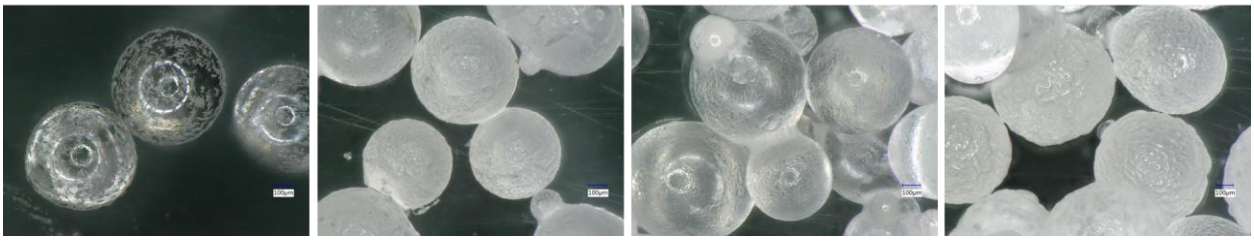


**Figure 3. Picture of glass beads being coated with the standard material (Irganox 1035).**

*3. The Third PBD Prototype*

The third prototype doser is very simple in structure, as shown in Figure 4. These PBDs consisted of a coil of stainless-steel tubing (ID 0.46 cm) packed with 1mm ceramic spheres coated with a new TOC standard material, 4-iodobenzoic acid (IBA). The vendor specified purity was just greater than 97.5%. However, the actual purity based on its certificate of analysis was listed as 100.0%.

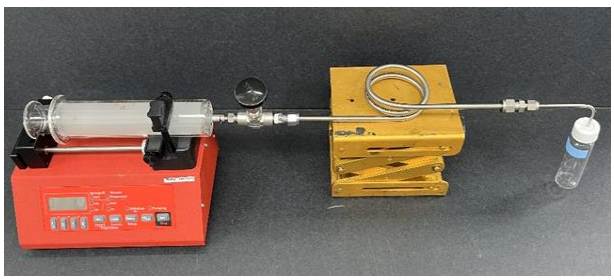


**Figure 4. The flow-through test setup of PBD #3-1.**

### B. Lessons Learned: Cleanliness

The earlier prototypes were built and tested without success before the current design (the third prototype). This section will document the lessons learned. However, the major lesson learned can be summarized into one sentence: cleanliness is key for low TOC applications. This has been a recurring theme in the PBD development process. Some lessons are obvious and are matters of establishing the best practice. Other lessons are less apparent but still directly related to the same theme.

*1. Having a Rigorous Cleaning and Verification Method*

Low TOC applications require a different level of cleanliness. A rigorous cleaning and verification method must be established before any meaningful experiments can be conducted. It is crucial to thoroughly clean everything and verify its cleanliness, such as soaking parts in ASTM II reagent water and measuring its TOC increase over time.

*2. Building with Clean Parts that Would Not Leach TOC*

After the cleaning and verification process was established, it became clear that some parts leach TOC, even after they were cleaned. They were eliminated from the hardware material and test setup. Almost all plastic parts leach TOC. Use only stainless steel or glass parts, and use fewer parts when possible. Earlier test setups included a plastic syringe, used with the syringe pump, a plastic cartridge, used for the packed bed, and with plastic tubing. After the rigorous cleaning and verification method was established, they were identified and quickly replaced. Then, the stainless-steel cartridge (packed bed) was replaced with a simpler stainless steel tubing packed bed, to reduce the number of the components.

*3. Packing Media*

Glass, ceramic, and stainless steel (316L) do not leach TOC after thoroughly cleaning. However, they still leach ions. This ion leaching can impact effluent conductivity, making it challenging to use TOC analyzers that rely on conductivity sensors to measure low levels of TOC. This is particularly true for packing media with a large surface area. Coating the media beads with the standard material does not eliminate the problem, so for our testing it was necessary to switch to a TOC analyzer using an IR detector.

*4. Standard Materials*

The purity of the standard material used for the packed bed is critical to conducting a successful test within a reasonable time frame, i.e., for the system to reach a steady state output of TOC at the target concentrations. When possible, the any impurities should be identified, and their concentration should be considered to estimate the time it will take to clean the standard material in the packed bed before meaningful data can be collected. In general, it is recommended to use the highest purity standards available.

## V. Packed Bed Doser Tests

### A. Experimental

*1. Packed Bed Dosers (PBDs) with 4-Iodobenzoic Acid as TOC Calibration Standard*

Three packed bed dosers were built for testing. The PBDs consist of a coiled stainless-steel tubing (ID 0.46 cm) packed with 1mm ceramic spheres coated with a TOC standard material, 4-iodobenzoic acid (IBA).

The ceramic spheres used as the packing media in this version of PBD were Yttria Stabilized Zirconia (YSZ) Micro Milling Media (MSE Supplies). The YSZ spheres were coated with 4-Iodobenzoic acid (Sigma-Aldrich, Product #206547, Batch #BCCD6480) using a BUCHI Rotavapor R-210, with acetone as solvent. The specified purity of 4-Iodobenzoic was greater than 97.5%, but the actual analysis result was determined to be 100.0%, based on the gas chromatography (GC) area percent.[14]

*2. Test Setup*

A flow-through test was conducted by pumping deionized (DI) water at various flow rates through the PBD before effluent samples were collected and analyzed. A New Era (NE-1000) syringe pump with a 100 mL glass syringe (SYR-GL 100LL) was used to pump the DI water through the PBD at a set flow rate. The DI water used for testing was ASTM Type II reagent water, produced by a Barnstead Smart2Pure water purification system, with resistance greater than 18.0 megohm-cm (MΩ-cm). The TOC concentrations of the effluent samples were analyzed using a Shimadzu TOC-L with an autosampler. To help with the IBA dissolution equilibration, DI water was pumped through

the tubing at 0.08 mL/min overnight before sample collection was initiated at the targeted flow rates. Additionally, to reduce temperature variation effects on the solubility of the IBA, the PBD was placed in a Grant W14 water bath in later experiments.

## B. Flow Through Test Results

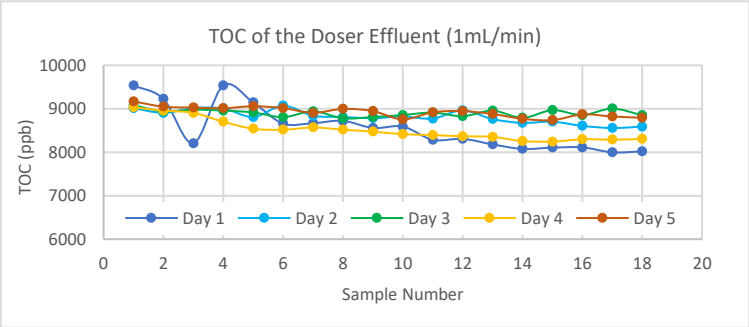
Three of the Prototype 3 PBDs were built for flow through testing. The first one (length 69 cm, ID 0.46 cm) was tested without thermal control, and the second and third PBDs (length 100 cm, ID 0.46 cm) were built for testing with thermal control.

### *1. Preliminary Test at 1 mL/min without Thermal Control (PBD #3-1)*

PBD prototype #3-1 was built to carry out the preliminary test. Figure 4 shows the test setup consisting of a syringe pump with a glass syringe, a valve, the PBD (#3-1), and the sample collection vial. This PBD was tested at room temperature, without additional thermal control.

The flow-through test was carried out at 1 mL/min for 5 days, with DI water pumped through the tubing at 0.08 mL/min overnight before starting the sample collection. Each day, the overnight effluent, and effluent samples (about 24 mL) were collected and analyzed using the Shimadzu TOC-L with an autosampler.

The result of the 1 mL/min flow-through is plotted and shown in Figure 5, along with the average value, standard deviation, relative standard deviation (RSD), and the range of the data for each day provided in the corresponding table. After the first day, the effluent TOC levels are relatively consistent (RSD < 3%). The data from Day 1 is higher, likely due to the slight impurity being cleaned out from the standard material at the beginning of the test.




| TOC (ppb) | Day 1 | Day 2 | Day 3 | Day 4 | Day 5 |
|---|---|---|---|---|---|
| Average | 8552 | 8818 | 8903 | 8509 | 8927 |
| Std Dev | 494 | 151 | 81 | 237 | 117 |
| RSD | 5.8% | 1.7% | 0.9% | 2.8% | 1.3% |
| Range | 1539 | 512 | 301 | 789 | 431 |

**Figure 5. The PBD (#1) flow-through test result of PBD #3-1 at 1 mL/min.**

### *2. 0.4 mL/min Test with Thermal Control (PBD #3-2)*

Figure 6 shows the test setup for the 0.4 mL/min flow-through test with PBD #3-2. The test setup consists of a syringe pump with a glass syringe, a valve, the PBD (#3-2), the sample collection vial, and the water bath.

This PBD was tested for two weeks, the first week was spent running some trials of temperature control with the water bath, while the second was run at 27 °C.

Each week, the 0.4 mL/min flow-through test was carried out for 4 days, with DI water pumped through the tubing at 0.08 mL/min overnight before sample collection at 0.4 mL/min flow rate.

Each day, the overnight effluent and effluent samples (about 24 mL) at 0.4 mL/min were collected and analyzed using the Shimadzu TOC-L with an autosampler. During the first week, the effluent samples were analyzed sequentially in the order they were collected, without DI flushes in between. In the second week, after day 2, DI flushes were added between effluent samples, in order to improved TOC measurement accuracy, by reducing TOC carried over from previous samples. One DI flush was added for day 3 samples, and three DI flushes were added for day 4 samples.

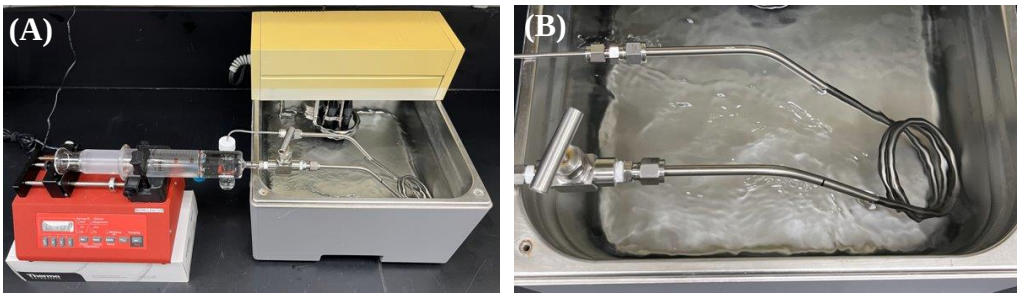
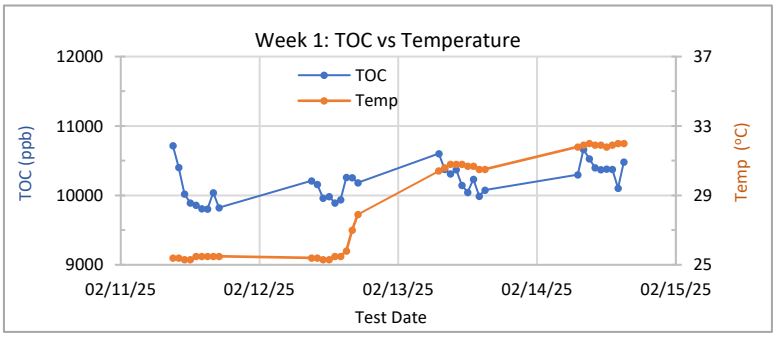



**Figure 6. (A) The flow through test set up of PBD #3-2, and (B) Close-up image of PBD.**

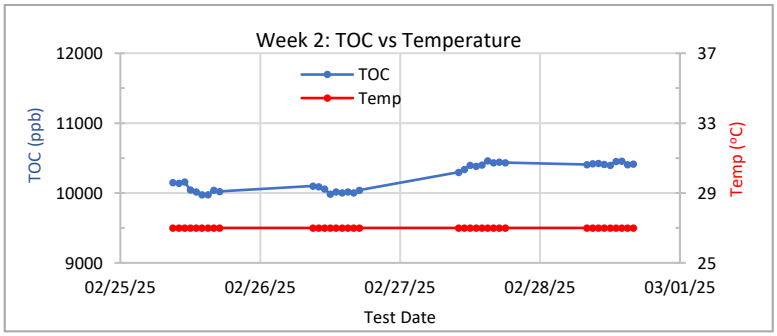
The results of the 0.4 mL/min tests during the two weeks are plotted as shown in Figure 7 and Figure 8, along with the average value, standard deviation, relative standard deviation (RSD), and the range of the data for each day provided in the corresponding tables. The data from Week 2 has better consistency (RSD: 0.2% to 0.7%): than that of Week 1 (RSD: 1.4% to 3.0%). This is likely due to better temperature control in Week 2.




| Week 1 TOC (ppb) | Day 1 | Day 2 | Day 3 | Day 4 |
|---|---|---|---|---|
| Average | 10042 | 10095 | 10240 | 10401 |
| Std Dev | 299 | 139 | 185 | 146 |
| RSD | 3.0% | 1.4% | 1.8% | 1.4% |
| Range | 915 | 370 | 611 | 557 |

**Figure 7. The PBD (#3-2) test result at 0.4 mL/min during Week 1.**

In Week 2, the data consistency of Day 4 (RSD 0.2%), with three DI flushes, is the best for the week. This indicates adequate flushing between samples is needed to improve TOC measurement accuracy. This is possible due to some sample deposition in the tubing, with multiple samples flowing through continuously. DI flushing is adopted for future sample analysis.




| Week 2 TOC (ppb) | Day 1 | Day 2 | Day 3 | Day 4 |
|---|---|---|---|---|
| Average | 10060 | 10036 | 10399 | 10422 |
| Std Dev | 68 | 38 | 50 | 19 |
| RSD | 0.7% | 0.4% | 0.5% | 0.2% |
| Range | 184 | 114 | 166 | 60 |

**Figure 8. The PBD (#3-2) test result at 0.4 mL/min during Week 2.**

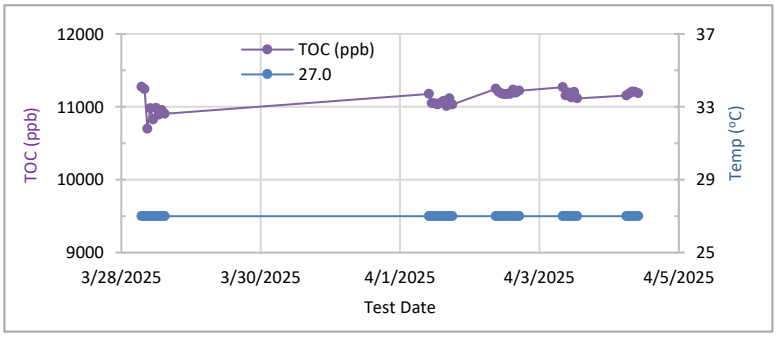
*3. Variable Flow Rate Test with Thermal Control (PBD #3-3)*

Figure 9 shows the test setup for the flow-through tests with PBD #3-3. This PBD was built for better thermal control; the coil cartridge being fully immersed in the water.

**Figure 9. The test setup of the flow-through tests of PBD #3-3.**

This PBD was tested first at 0.4 mL/min for more than a week, then it was tested at variable flow rates (1, 2, 4, 8, and 16 mL/min). The tests were done at 27 °C, with DI water pumped through the tubing at 0.08 mL/min overnight before sample collection. Each day, the overnight effluent and effluent samples (about 24 mL) were collected and analyzed using the Shimadzu TOC-L with an autosampler. All the effluent samples were analyzed with three DI flushes between samples.

The results of the #3-3 PBD 0.4 mL/min tests are plotted in Figure 10, along with the average value, standard deviation, relative standard deviation (RSD), and the range of the data for each day provided in the corresponding table. The data from Day 2 shows good consistency (RSD: 0.2% to 0.5%), similar to the result of PBD #3-2. The data from Day 1 is higher, likely due to the slight impurity being cleaned out at the beginning of the test.




| TOC (ppb) | Day 1 | Day 2 | Day 3 | Day 4 | Day 5 |
|---|---|---|---|---|---|
| Average | 10973 | 11066 | 11200 | 11178 | 11186 |
| Std Dev | 173 | 49 | 26 | 52 | 18 |
| RSD | 1.6% | 0.4% | 0.2% | 0.5% | 0.2% |
| Range | 575 | 166 | 75 | 154 | 51 |

**Figure 10. The PBD (#3-3) test result at 0.4 mL/min.**

The result of the variable flow rate for PBD #3-3 test is plotted and shown in Figure 11, along with the average value, standard deviation, relative standard deviation (RSD), and the range of the data for each day provided in the corresponding table. The effluent TOC levels are relatively consistent for each flow rate (RSD < 1.1%). These results suggest minimal flow rate effect up to 8 mL/min. The effluent TOC at 16 mL/min is slightly lower, by about 5%.

There was also observed a larger data variation (RSD) at higher flow rates. This is likely because, at higher flow rates the syringe needs to be changed more frequently. Frequent syringes change out interrupts the flow and leads to less stable dosing. Overall, these results indicate the effluent TOC of this PBD design is stable around the target flow rate (0.4 ml/min) and is not highly sensitive to flow rate fluctuations.

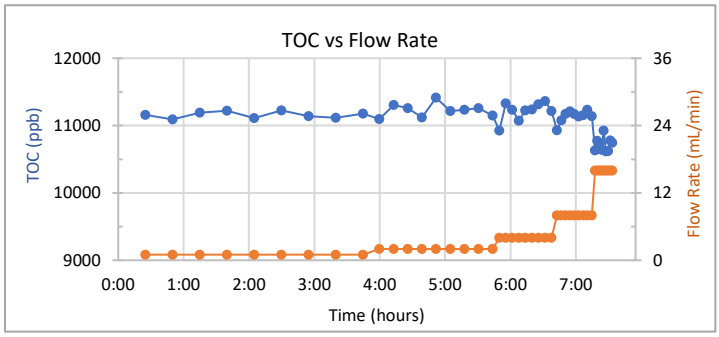
## C. Discussion and Summary

Three Packed Bed Dosers (PBDs) with 4-Iodobenzoic Acid as TOC calibration standard were built and evaluated for their dosing behavior. The simple design of the stainless-steel coiled tubing design works well. The high purity of the standard material contributes to the success of the proof-of-the-concept tests, as the effluents of these PBDs reach steady state quickly (in a couples of days).

Not surprisingly, thermal control is important to establish stable effluent TOC dosing due to the effect of the temperature on solubility. More detailed studies will be carried out to establish the correlation between the temperature and the effluent TOC level for each PBD; thus, the effluent TOC level can be precisely predicted given the temperature of the input water.

Flow rate variation has only minimal effect on the effluent TOC until the flow rate is above 8mL/min. This is likely do to the effluent concentration is close to the saturation concentration of the standard material with current PBD configuration at lower flow rates. This is advantageous for the targeted application of the PBDs.

It was also found that, for the TOC analysis of the effluents, flushing between samples can help to improve TOC measurement accuracy. DI flushing is adopted for sample analysis, and will be used to develop concept of operation of these PBDs.




| Flow Rate (mL/min) | 1 | 2 | 4 | 8 | 16 |
|---|---|---|---|---|---|
| Average TOC (ppb) | 11159 | 11227 | 11214 | 11136 | 10718 |
| Std Dev (ppb) | 45 | 93 | 129 | 85 | 97 |
| RSD | 0.4% | 0.8% | 1.1% | 0.8% | 0.9% |
| Range (ppb) | 129 | 316 | 434 | 304 | 310 |

**Figure 11. The PBD (#3-3) test result at variable flow rates: 1, 2, 4, 8, and 16 mL/min.**

## VI. Overview and Future Plans

### A. Overview

A passive dosing device has been designed for a potential online TOC calibration method for exploration-class Total Organic Carbon Analyzers. Several doser prototypes were built, and a proof-of-concept testing was successfully conducted. The most important lesson learned is that cleanliness is critical for the low TOC standard doser development, design and testing. This means having a rigorous cleaning and verification method, eliminating any part that leaches TOC, and only using standard materials of the highest purity.

### B. Future Plans

Further developments include extended temperature effect tests, pressure drop verification, building doser prototypes at other TOC levels. Ultimately, the project goal is to demonstrate the proposed system for on-orbit calibration using long and stable shelf-life TOC standards and incorporating methods for accurate instrument calibration and measurement of TOC in high background spacecraft waters.

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