

# Development of the Miniature Robotic Electrodialysis (MR ED) System for Small-Scale Desalting of Liquid Samples with Recovery of Organics

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## Key Points:

- Liquid sampling on ocean worlds will require desalting, as salts can hinder the measurement capabilities of instruments.
- Desalting by electrodialysis retains organic material, but existing technology requires miniaturization to be feasible for use on missions.
- The Miniature Robotic Electrodialysis system has recovered between 55-77% of the organic material after removing 97-99% of the salts.

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## Abstract

While liquid environments with high salt content are of broad interest to the Earth and Planetary Science communities, instruments face challenges in detecting organics in hypersaline samples due to the effects of salts. Therefore, technology to desalt samples before analysis by these instruments would be enabling for liquid sampling on missions to Mars or ocean worlds. Electrodialysis (ED) removes salt from aqueous solutions by applying an electric potential across a series of ion-selective membranes, and is demonstrated to retain a significant percentage of dissolved organic molecules (DOM) in marine samples. However, current electrodialysis systems used for DOM recovery are too large for deployment on missions or for use in terrestrial fieldwork. Here we present the design and evaluation of the Miniature Robotic Electrodialysis (MR ED) system, which is approximately 1/20th the size of heritage instruments and processes as little as 50 mL of sample at a time. We present tests of the instrument efficiency and DOM recovery using lab-created solutions as well as natural samples taken from an estuary of the Skidaway River (Savannah, GA) (Verity, 2002) and from South Bay Saltworks (San Diego, CA) (Survey, 2011; Roseman & Watry, 2008). Our results show that the MR ED system removed 97-99% of the salts in most samples, with an average DOC recovery range from 53 to 77%, achieving similar capability to tabletop instruments. This work both demonstrates MR ED as a possible field instrument and increases the technology readiness level of miniaturized electrodialysis systems for future missions.

## Plain Language Summary

Liquids on other planetary bodies, such as Mars or the icy moons of the outer planets, are important sampling targets for the search for life. Salts help preserve these liquids but can clog small fluidic systems and alter and inhibit the capabilities of precision chemical measurement instruments. Therefore, a key technology development for liquid sampling on ocean worlds is a robust system to desalt samples before they are analyzed by these instruments. Electrodialysis (ED) is a process that removes salts from a sample using a voltage applied across charged membranes to separate the salts' ions from the solution. It has been used in laboratory systems to desalt aqueous solutions while recovering the dissolved organic carbon that would be desirable to measure after the process. However, current systems require further miniaturization and autonomy development to be suitable for deployment on spacecraft. We present the Miniature Robotic Electrodialysis (MR ED) system that has successfully removed 97-99% of the salts in samples and recovered between 53 to 77% of the dissolved organic matter, which is comparable to larger commercial systems at approximately 5% the size.

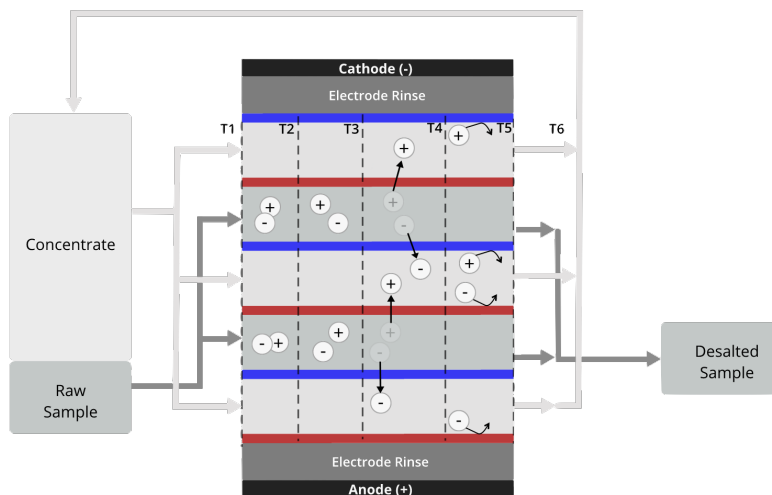
## 1 Introduction

The search for life in our solar system, both past and extant, is a primary goal of NASA missions (National Research Council, 2011). Targets of interest include subsurface habitable niches on Mars (Jakosky et al., 2003; Westall et al., 2013), and "ocean worlds" such as the moons Europa, Enceladus, and Ganymede (Hendrix et al., 2018). Potential biologically-relevant materials such as carbon-bearing compounds and even possible metabolic biproducts have been detected or implicated on Mars (Li et al., 2015; Niles et al., 2013; Wray et al., 2016), Europa (Carlson et al., 2009) and Enceladus (Glein et al., 2015; Glein & Waite, 2020; Waite et al., 2017). Particularly for the ocean worlds, future in situ missions would greatly enhance our understanding of the composition of their surfaces and oceans (Hendrix et al., 2018; Lunine, 2017). This increasingly drives interest in developing instruments and sample handling systems that are capable of interrogating these worlds for evidence of habitable environments and life (Committee on the Planetary Science and Astrobiology Decadal Survey et al., 2022).

Organic materials are the building blocks of life on Earth and are therefore their detection is highly prioritized on both active and planned spacecraft missions. Detecting organics in planetary environments has proved nonetheless challenging. Since planetary environments such as Mars’ surface and Europa’s oceans may have low bioburden, methods to enhance the signal from organics are needed. Amongst the most difficult challenges may be the confounding effects of salts. For example, modern evidence for brines on Mars is accompanied by the detection of perchlorate salts (Hecht et al., 2009; Ojha et al., 2015), and geologic evidence for ancient salty, acidic environments abounds (Rapin et al., 2019; Wang et al., 2018). Analyses completed by the Sample Analysis at Mars (SAM) have used a mass spectrometer and gas chromatograph to search for organic species; however the presence of perchlorates in Martian soil has been theorized to have affected their detection (Franz et al., 2014; Mahaffy et al., 2012). Perchlorates can promote the combustion of organic compounds under high temperatures, which occur during the gas processing of solid samples (Li et al., 2015; Mahaffy et al., 2012; Navarro-González et al., 2006; ten Kate, 2010) which may confound measurements of organic molecules and/or destroy or alter such molecules in situ (S. A. Benner et al., 2000; Lewis et al., 2021).

Salts may also confound detection of organics on ocean worlds. Europa is the target of the Europa Clipper (Howell & Pappalardo, 2020) and Jupiter Icy Moons Explorer (Witasse & JUICE Teams, 2020) as well as possible surface missions that would characterize the composition of the surface materials and search for organics (Hand et al., 2021, 2017) and subsurface mission concepts that seek to access and explore the global liquid water ocean beneath Europa’s thick ice shell (Kivelson et al., 2000; Bryson et al., 2020; B. Schmidt et al., 2021; Stone et al., 2018; Zacny et al., 2018). Predictions for the salt content and composition in Europa’s ice shell and ocean are varied but include NaCl and MgSO<sub>4</sub> salts (Carlson et al., 2009; McCord, 2000; Trumbo et al., 2019) at brackish to saturated concentration (Buffo et al., 2020; Chivers et al., 2021; Hand & Chyba, 2007; Kivelson et al., 2000; B. E. Schmidt, 2020; Zolotov & Shock, 2004; Zolotov & Kargel, 2009). In addition to the ocean, there is potential for pockets of brine within the ice shell that could vary strongly in salinity depending upon their detailed evolution and age (Chivers et al., 2021; Collins & Nimmo, 2009; B. E. Schmidt et al., 2011). Potential preservation of organic molecules within these brines makes them a target of high interest for life detection (Bryson et al., 2020; Fisher et al., 2021; Lawrence et al., 2021; Merlino et al., 2018), however their salt content presents challenges to instruments for detecting organics.

Increasingly, sampling and sample handling systems for planetary missions that seek to detect evidence of life include multiple “phases” of measurements by suites of instrumentation with increasing sample processing complexity; some instruments require little to no processing, whereas others require extensive processing (Hand et al., 2021, 2017; Mahaffy et al., 2012). This latter category of instruments includes mass spectrometry and nanopore sequencing, both of which require direct contact and interaction with a sample within the spacecraft (Hand et al., 2021, 2017; Lawrence et al., 2021). In order to measure organics and search for other biomarkers, future missions will require the ability to both concentrate material and remove confounding salts that can alter such chemical measurements, in particular mass spectrometry that is a cornerstone of landed missions (Franz et al., 2014; Grubisic et al., 2021; Hand et al., 2017). Compositional measurements with mass spectrometry involve ionizing the sample molecules, which is complicated by high concentrations of background ions in the sample, such as salts. Mass spectrometers have a limited volume of ions that can be analyzed, and unwanted salt ions can effect interactions that can diminish the sensitivity and accuracy of the instrument, and reduce the ability of the mass spectrometer to detect and quantify molecules of interest (Zeichner et al., 2022). Salts can also impede the ionization of biological molecules through suppression or breakdown of the molecule during ionization (Donnelly et al., 2019; Duncan et al., 2019; Metwally et al., 2015). Moreover, as in situ sequencing of samples becomes possible onboard spacecraft, extraction efficiency of DNA by nanopore sequencers is greatly reduced in solutions with high salt concentration (Weng et al., 2019). Thus



**Figure 1.** An illustration of the electrodialysis process. Electrodes on either side of the stack provide the voltage potential and are in contact with a circulated electrode rinse. (T1) Sample and concentrate solutions are fed into the electrodialysis stack. (T2) These solutions alternate between anion-selective membranes (blue) and cation selective membranes (red). (T3) Ionic salt compounds are split by the voltage potential applied across the stack. (T4) Ions are pulled across their respective membranes into the concentrate channels. For example, positively charged ions are drawn towards the negatively charged cathode through the cation-selective membranes. Similarly, negatively charged anions are pulled through the anion-selective membranes towards the anode. (T5) The positively charged ions are trapped in the concentrate channel as they cannot pass through the anion-selective membrane; negatively charged ions are similarly trapped as they cannot pass through the cation-selective membrane. (T6) The concentrate channels are circulated with an external reservoir, and the desalted sample is either circulated for further desalting or removed from the system. The arrangement of membranes, flow channels and electrodes deplete the sample of dissolved salts during sample processing.

it has been recommended that methods to remove salts in milliliter to microliter-scale samples while preserving organic compounds within the sample be developed, in order to create water samples suitable for analytical life detection techniques that are confounded by high salinities (Lawrence et al., 2021).

On Earth, characterizing the abundance of organics in the ocean is greatly improved by desalting (Gurtler et al., 2008; Mopper et al., 2007). Electrodialysis (ED) is a technique employed by oceanographers to remove salt while retaining and concentrating organic molecules of interest for analysis. Electrodialysis uses an electric potential applied across a stack of separated flow channels typically containing two different aqueous solutions — a ‘sample’ solution from which ions are removed and a ‘concentrate’ solution into which ions travel. These channels are separated by alternating anion and cation exchange membranes, as shown in Figure 1, which allow negatively and positively charged ions to pass through, respectively, while preventing movement of oppositely charged ions. The electric potential across the alternating membranes pulls the ions from the sample flow channel into the adjacent flow channel where the arrangement of the membranes traps the ions in the receiving solution. Typically, ED systems also have an additional flow channel that circulates a solution in contact with the cathode and anode, called the



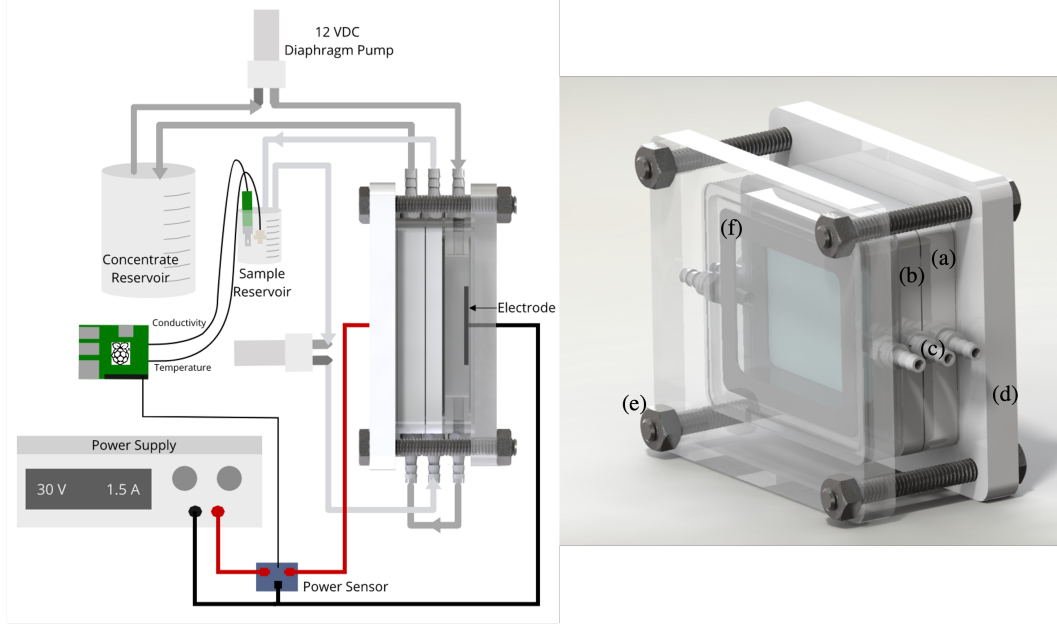
electrode rinse. This additional channel reduces unwanted interactions between the salts pulled from the sample solution and the electrodes.

Electrodialysis is ideally suited for sample preparation as it has been shown to efficiently remove salts from seawater and brines while retaining a high percentage of dissolved organic molecules in laboratory-scale setups. Recovery of organic molecules is typically measured via the dissolved organic carbon (DOC) concentration of the sample before and after processing with electrodialysis (R. Benner & Strom, 1993; Grasshoff et al., 2009). In coastal seawater samples and phytoplankton cultures 70% of the DOC is retained in samples processed with laboratory-scale electrodialysis systems, while 99.7% of the salts are removed (Chambers et al., 2016; Gurtler et al., 2008; Koprivnjak et al., 2006; Vetter et al., 2007), although lab-created samples show that some organic molecules (eg. glucose, vitamin B12) can near complete recovery after electrodialysis (>90%) (Chambers et al., 2016). This recovery is typically much better than other techniques to recover organic molecules from seawater such as extraction resins ( $\approx 50\%$ ) or ultrafiltration ( $\approx 30\%$ ) (Chambers et al., 2016). Combined reverse osmosis/electrodialysis processing has been proven to concentrate and desalt samples on a much larger volume scale (200 L) while retaining between 60-90% DOC in seawater samples (Vetter et al., 2007). The advantage of using reverse osmosis (RO) is to decrease the sample volume to concentrate the organic material; however, on smaller volumes electrodialysis alone can recover as much DOC as the combined process. These successful electrodialysis systems are large and have been used to process between 0.5 L and 200 L of sample; however, miniaturized systems require further development to achieve similar recovery, and require design changes to function as a part of a science package deployment on a spacecraft. Minimization of sample volumes has many advantages including reduction of instrument size and power requirements if the science value can be preserved. Additionally, miniaturization is advantageous for making the process field portable for investigations in remote locations on Earth by reducing the logistics of collecting large volumes of sample. Field sampling and analysis has relevance in many environments, such as deployment on oceanographic investigations, as well as investigating samples from hypersaline environments, which have the potential to be analogs for ocean worlds (Buffo et al., 2021; Klempay et al., 2021); however, their high concentrations of salts are detrimental to instrument processing.

The handling of liquid samples is the next frontier of planetary exploration. Given the prevalence of compelling planetary environments to explore that contain moderate to high concentrations of salts, the development of desalting as a part of sample preparation is critical. Relevant to planetary exploration, laboratory electrodialysis systems developed for use on Earth are large and require manual operation, and thus, are not well-suited to fly on a planetary mission. To realize the organic preservation of ED systems on a scale appropriate for planetary missions, we designed a miniaturized, robotic electrodialysis system (MR ED), and tested the instrument to increase its technology readiness level (TRL) for consideration on a future mission.

## 2 Materials and Methods

We sought to develop a miniaturized electrodialysis system that removes salts from a sample solution while minimally disrupting organics and maintains a compact design to progress towards desalting in challenging planetary environments. To meet these goals, we implemented a design shown in Figure 2. The Miniature Robotic Electrodialysis system uses a single cell membrane pair; that is, there is one pair of ion-exchange membranes and only one sample flow chamber in the system. The exchange membranes separate a sample channel from two combined concentrate/electrode rinse channel, as shown in Figure 2. The channels are made of machined Delrin and 3D-printed UV-sensitive resin, which is inert after curing and allows for printing unique shapes such as interior fluid routing and hose barb connectors. The sample chamber holds approximately 25 mL, and the combined electrode rinse/concentrate chambers hold approximately 40 mL of fluid. Rather



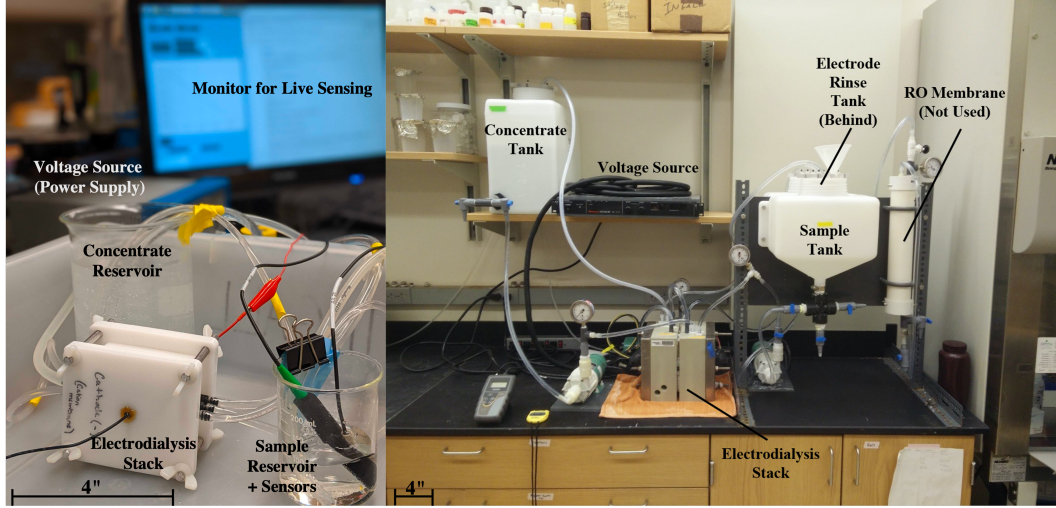
**Figure 2.** The Miniaturized Robotic ElectroDialysis system. To the left, a schematic of the MR ED setup. Excess concentrate and sample are contained in separate reservoirs, with conductivity and temperature sensors in the sample reservoir. Pumps continuously circulate the fluids, and a power supply provides the voltage potential across the electro dialysis stack. To the right, a model of the MR ED system, which holds approximately 40 mL in the combined electrode rinse/ concentrate chambers (a) and 25 mL in its sample chamber (b). Hose barb connectors (c) thread into the separate channels to allow fluid routing. The assembly is held together using the endcaps (d) through which electrodes access using thru holes, and threaded screws and nuts (e) to maintain an adjustable tight seal. Between each piece in the assembly there is rubber gasket material (f) to prevent leaks and ion-exchange membranes between each concentrate chamber and the sample chamber.

than use separate electrode rinse channels, MR ED's electrodes are in direct contact with the concentrate. This follows from MR ED's intended applicability for use on a planetary mission for which mass must be conserved, and thus a separate volume of electrode rinse is not required. To avoid corrosion of the electrodes, the electrodes are a platinized titanium mesh, which is resistant to corrosion and oxidation (Hayfield, 1983).

Ion-exchange membranes are used between each chamber to selectively allow only cations or anions to pass. The ion-exchange membranes used here are anion Fumasep FAS-PET-130 and cation Fumasep FKS-PET-130 (*Fumasep - ion exchange membranes for water treatment*, 2020), and are laser cut to fit MR ED's form factor. The selection of ion exchange membrane is driven by parameters including the membrane's thickness, permselectivity, and area resistance. The thickness of the membrane affects its conductivity as well as its susceptibility to adsorption of organics, or fouling, which can increase the membrane's resistance and thus reduce its transfer efficiency (Lindstrand et al., 2000). The membrane's permselectivity is a measure of its ability to differentiate between anions and cations (Luo et al., 2018), and the area resistance is a measure of how much current can flow across the membrane in the presence of a voltage potential (Galama et al., 2016). The membranes we used with MR ED have heritage use in laboratory-scale electrodialysis systems, and have high specific area resistance and selectivity. They are reinforced with polyester, which increases the thickness compared to similar membranes, but provides resistance to degradation by acids, bases, and oxidation.

To assemble the system as shown in Figure 2, the chambers are stacked with membranes between them and rubber gaskets on either side of each membrane. Rubber gaskets are additionally used against the endplates to seal the concentrate channels. Electrodes, which are connected to the endplates with an epoxy-sealed hole to allow a wire through the endplate, are connected to the power supply. Four threaded rods connect the endplates with thumb screws on either end, so that the assembly is tightly but adjustably sealed. Hose barb connectors screw into each chamber to connect to the tubing that routes the fluids. The sample fluid is routed using silicon tubing from its monitoring reservoir to a 12 VDC diaphragm pump, which circulates the sample to the sample chamber and back to the reservoir. The concentrate fluid is first routed from its reservoir beaker through a second pump, then to the concentrate chambers in series before it returns to the reservoir. Circulating the fluid in this way greatly increases the efficiency of desalting by electrodialysis by keeping the fluid well-mixed. A well-mixed fluid keeps the ionic composition near the membrane surfaces replete with ions. In contrast, in static fluid ions are rapidly depleted at membrane surface which decreases desalting efficiency and results in the hydrolysis of water molecules that impacts sample pH.

We selected a Raspberry Pi computer to record and display information gathered from the sensors using a custom graphic user interface. Using a Raspberry Pi allows for further development to increase the system's autonomy or sensing capabilities while maintaining a compact footprint. It additionally provides convenient interface to the sensors. MR ED uses a temperature sensor (AtlasScientific Micro PT-1000 Temperature Probe) and conductivity sensor (AtlasScientific Mini Conductivity Probe K 1.0) to monitor the salinity of the sample as well as an Adafruit INA260 sensor to measure the voltage and current applied across the cells. Monitoring the voltage and current throughout processing allows the operator to see issues in the processing that is hidden inside the assembly; for example, precipitating salts result in noticeable difference in the power response compared to that of a smoothly running process. The sensing locations can be seen in the schematic in Figure 2. We used a BK Precision DC Regulated 1670A benchtop power supply capable of a 30 V output. We imposed a limit of 1.5 A using the power supply to avoid exceeding the limiting current density of the membranes, above which increased potential does not increase the transport of ions across the membranes, and operation can damage the membranes.



**Figure 3.** A comparison of the MR ED system with its contemporary, from Chambers et al. (2016). MR ED processes between 50 and 100 mL of sample, whereas the larger system has been used to process between 0.5 and 200 L of sample. The similar components of the two systems are labeled for comparison. MR ED is approximately 1/20 the size of its laboratory contemporary, based on the sum of the volumes of the systems' components.

The testing process for each type of sample and concentrate, which are detailed in Table 1, begins with an initial circulation of the sample and concentrate prior to applying power to the electrodes. The sample is then emptied from the reservoir and circulated twice before the final circulation. This is done to rinse the membranes and tubing with the new solutions – organic content may be absorbed onto the membrane during this circulation or may be dislodged from absorption during a previous test, so circulation is necessary before the initial DOC analysis. After circulation, four milliliters are taken from the sample and concentrate for the initial DOC analysis before power is applied. We employ a Shimadzu TOC-VCSN total organic carbon analyzer to analyze the DOM recovery of each sample processing run, which measures the organic carbon content in a sample taken from the solutions (R. Benner & Strom, 1993; Grasshoff et al., 2009). This provides a starting dissolved organic carbon (DOC) concentration to be used for comparison for recovery. Samples with low expected DOC content are analyzed undiluted, while samples with higher expected DOC content, such as natural samples, are diluted up to 40-fold before analysis to be better conditioned for the instrument. The power is applied to the system until the sample's conductivity falls below 1 mS/cm, which corresponds to  $\sim 8$  mM for NaCl solutions, after which four milliliters of sample and concentrate are once again taken for the final DOC analysis.

MR ED's design focus is the miniaturization of an electrodialysis system for consideration for use on a future instrument payload. The benchtop system we have created is a fraction of the size of established systems, as exhibited in Figure 3, and has an added benefit of low complexity and using cells that are either 3D printed or are easy-to-machine pieces makes the system easily replicable, and thus makes it accessible for a wide range of uses. The design allows flexibility in the system for adding additional cell pairs to increase sample volume or desalting efficiency, or to include an additional electrode rinse channel. Further miniaturization of the system can be achieved by reducing the size of the chambers, which will reduce fluid volumes in each channel. To improve the desalting efficiency, we have included constant circulation of all fluid to promote mixing of the ion-depleted and ion-enriched sample nearest to the membranes, and the thick channels

**Table 1.** Types of solution used for the sample and concentrate during testing

Solution Description	Solution Name	Notes
0.5 N NaCl, 200 ppm glucose	Sample 1	Lab-created
Skidaway River (GA, USA)	Sample 2	Estuarine seawater
South Bay Salt Works Site 11 Brine	Sample 3	Primary salt is NaCl
South Bay Salt Works Site 5 Brine	Sample 4	8x Dilution with MilliQ water, primary salt is MgCl <sub>2</sub>
10 mS/cm Na <sub>3</sub> PO <sub>4</sub>	Concentrate 1	Lab-created
20 mS/cm Na <sub>3</sub> PO <sub>4</sub>	Concentrate 2	Lab-created

of fluid further promote this mixing. We eliminated the use of the electrode rinse to reduce the complexity specifically with the motivation for planetary mission use, which additionally improves the terrestrial field-portability of the device. With the ambition of the device being used autonomously, we included a suite of sensors connected to a Raspberry Pi, which can be used in the future to control an integrated power system and pumps. We have tested the device with as little as 50 mL of sample, which is more than 10 times smaller than that of commercially available systems (Chambers et al., 2016; Koprivnjak et al., 2006).

### 3 Results and Discussion

We designed the Miniature Robotic Electrodialysis system to desalt samples representative of those that would be expected on Europa. In the absence of specific salinity measurements on Europa, we tested the system with samples with composition similar to Earth seawater to samples many times more saline than seawater. Key results from benchtop testing of the MR ED system are shown in Table 2, and descriptions of the sample and concentrate solutions that were used are in Table 1. Initial tests to verify MR ED's functionality included circulating sample and concentrate without power applied to verify that the system had no leaks, as well as test of the diffusion of salts through the membranes without power applied. This latter test used a sample of 1 M NaCl and a lightly salty (2 mS/cm) NaCl solution as the concentrate; when left in the system, ions will naturally diffuse from the higher concentration sample channel to the lower concentration concentrate channels. Without circulation, the sample only was desalted to 58% its original salinity after 24 hours; circulation can increase the efficiency by replenishing the ions in the fluid nearest to the membranes. Applying a voltage potential across the membranes additionally increases the speed of the process and promotes further desalting of the sample.

We conducted Tests 1 and 2 to initially assess the desalting capabilities and DOC recovery of the MR ED system. In Test 1, we prepared 300 mL of Sample 1, created from a 0.5 M NaCl solution spiked with 186 mg of glucose to achieve a concentration of 200 ppm glucose. Both concentrate and sample solutions began at a temperature of 21 °C; however, the temperature rose quickly as the power was applied. The temperature of the sample after desalting the sample from 42.1 mS/cm to 0.978 mS/cm was 37.5 °C, and the temperature of the concentrate was 34.2 °C. The concentrate's temperature did not increase as much as that of the sample, as we used a larger volume of concentrate than sample; 150.5 mL of the prepared sample solution was used in comparison to 1000 mL of concentrate. Throughout the test, the Raspberry Pi adjusted the conductivities for



**Table 2.** Results from benchtop system tests with initial and final conductivity, % DOC recovered, and calculated salinity (based on temperature and conductivity data) for NaCl-based solutions. Data available from Bryson et al. (2022)

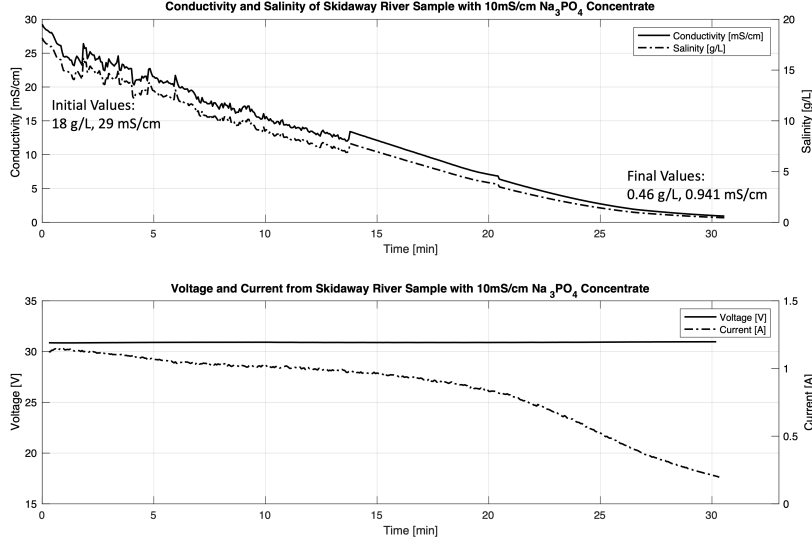
Test	Sample	Initial conductivity [mS/cm] (Salinity [g NaCl/L])	Final conductivity [mS/cm] (Salinity [g NaCl/L])	DOC % recovery	Concentrate	Notes
Test 1	Sample 1	42.1 (27.1)	0.978 (0.487)	53%	Concentrate 1	No temperature control
Test 2	Sample 1	40.2 (25.8)	0.996 (0.493)	69%	Concentrate 1	
Test 3	Sample 2	21.4 (12.9)	1.04 (0.517)	71%	Concentrate 1	
Test 4	Sample 2	26.3 (16.1)	0.928 (0.458)	72%	Concentrate 1	
Test 5	Sample 2	29.3 (18.2)	0.945 (0.466)	-	Sample 2	Testing with a higher salinity concentrate, but carbon analysis results were inconsistent
Test 6	Sample 2	29.3 (18.1)	0.899 (0.443)	67%	Sample 2	Testing with a higher salinity concentrate
Test 7	Sample 3	85.1 (61.1)	0.913 (0.451)	77%	Concentrate 2	Higher salinity concentrate used to speed process
Test 8	Sample 3	90.1 (64.5)	49.1 (32.2)	-	Sample 3	Testing with higher salinity concentrate. Significant precipitation necessitated premature termination
Test 9	Sample 4	72.76 (TDS 400 g/L) <sup>1</sup>	27.0	-	Concentrate 1	Decrease in current indicated low ion flow across membranes
Test 10	Sample 4	71.48 (TDS 400 g/L) <sup>1</sup>	27.1	53%	Sample 4	Testing with higher salinity concentrate. Significant precipitation necessitated premature termination

<sup>1</sup>Total dissolved solids measurement courtesy of (Klempay et al., 2021)

the temperature so that they could be read as conductivity at 25 °C, as temperature affects the solution's conductivity and would lead to inflated conductivity readings as the temperature increased. In this test, the current was initially limited at 1.5 A, and decreased as the sample lost its ions and became less conductive. The total DOC recovery for Test 1 was 53%, which is calculated from the final and initial DOC analyses, as well as the final and initial volumes of sample.

In Test 2, we created the same sample and concentrate solutions as in the first test. The initial conductivities of the sample and concentrate were 40.4 mS/cm and 10.4 mS/cm respectively. However, both solutions were stored in beakers within an ice bath before and during the test to address the temperature increase seen in Test 1. The initial temperature of the sample was 10.1 °C, and the initial temperature of the concentrate was 12.7 °C. In this test, the sample heated 3.4 °C from the applied current, but the temperature of the concentrate decreased to 12.1 °C – there was a large enough volume of concentrate that the current did not increase the temperature faster than the cooling the ice bath. In comparison to Test 1, the current never reached the imposed limit of 1.5 A – the initial current was 1.35 A, and decreased throughout the test to 0.25 A. Because both Tests 1 and 2 used the same sample solution, this difference in the current could be a result of the difference in the temperature of the solutions; a colder solution is less conductive, and thus supports less ion flow across it. The DOC recovery for Test 2 was 69% after the sample was desalted from 40.2 mS/cm to 0.996 mS/cm conductivity.

In addition to laboratory produced samples, we tested the system with natural samples that were sourced from the Skidaway River in Savannah, Georgia (USA). A total of two gallons of sample were gathered in June 2021 during high tide at (31.997222, -81.030500), an outlet of the Skidaway river across from Skidaway Institute of Oceanography. The Skidaway River is an estuarine river that derives its higher salinity from the ocean's tides, thus its salinity reaches its maximum during high tide (Verity, 2002). Two liters of sample were gathered and filtered to remove particles larger than 0.7 µm before they were tested with MR ED to prevent clogging the tubing, interior channels, and mem-

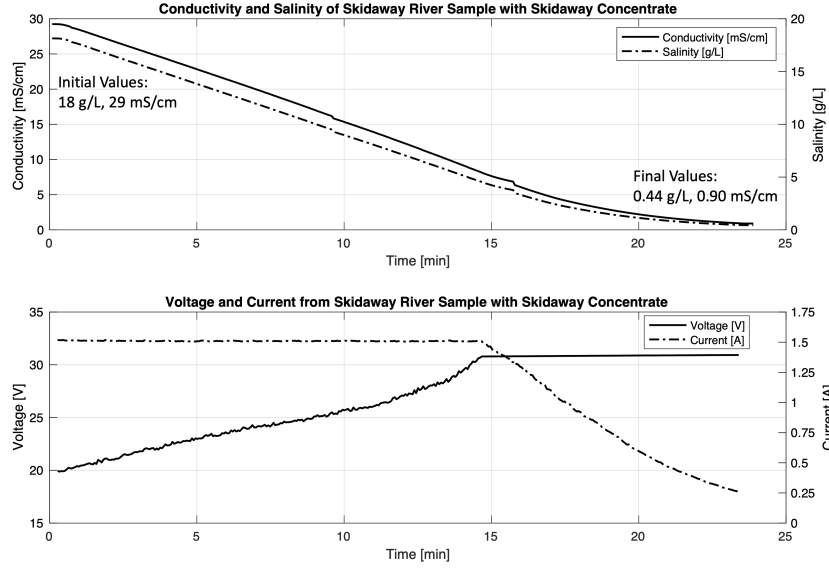


**Figure 4.** The processing of Sample 2 from the Skidaway River in Savannah, GA shows progressive desalting as power is applied across the membrane stack. In this experiment, the concentrate is a low salinity (initial conductivity of 10 mS/cm)  $\text{Na}_3\text{PO}_4$  solution. The solution was desalted to 1 mS/cm conductivity within 33 minutes, removing 97.4% of the salts. Using the  $\text{Na}_3\text{PO}_4$  solution provides a low salinity solution to transfer ions into (aided for a large portion of the processing by diffusion), and the current draw remains below the limit as the low salinity channels of the ED stack act as insulators.

branes. In planetary missions, pre-filtration would be a likely step prior to other processing (Lawrence et al., 2021), as is standard in ocean sampling. We processed these samples with Concentrate 1 and achieved an average of 72% DOC recovery. The conductivity, salinity – which was calculated using the Gibbs Seawater Toolbox from the measured conductivity and temperature (McDougall & Barker, 2011) – and power data from the process is displayed in Figure 4. The power data shows that the current began below the imposed limit at 1.5 A and decreased as the loss of ions made the sample less conductive, corresponding to the sample’s salinity decreasing. Current across the system can be related to the ion movement, so the higher current is an indicator of the faster desalting. As the sample’s conductivity approaches 0 mS/cm, the current decreases more quickly; the end of the desalting process takes much longer than its start as the lack of ions prevents current flow. From this we can conclude that although it is possible to desalt the sample below our chosen conductivity limit of 1 mS/cm, there is a trade space among final salinity, processing time, and DOC recovery.

On an in situ science package, a large quantity of concentrate would be needed for the duration of the mission; however, the need to carry this concentrate can be minimized by using the ambient water in its place. This is a difficult operation as the concentrate quickly becomes saltier than the sample that it is desalting, and it becomes more difficult for a power system to pull the ions into the saltier solution. In Tests 5 and 6, we used a 1 L volume of Sample 2 as the concentrate (see Table 1) to test this operation. We separated this volume from a 50 mL volume of Sample 2 that would be used as the sample. Both containers were placed in an ice bath, and the system was rinsed and circulated before power was applied. Immediately we noticed a difference in the power data from Tests 3 and 4, which can be seen in Figure 5 compared to Figure 4. When using

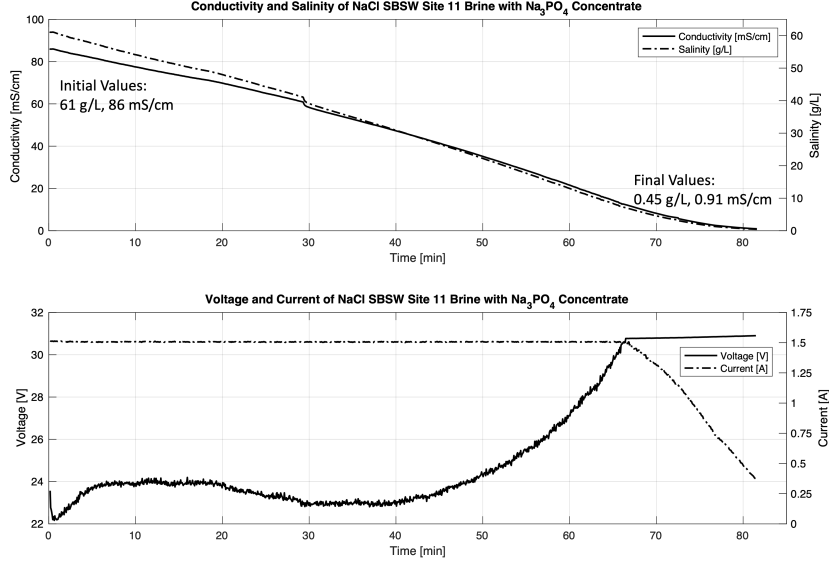




**Figure 5.** Processing of Sample 2 from the Skidaway River in Savannah, GA shows the desalting process in which 97.5% of the salts were removed. In this experiment, a separate container of this sample has been prepared to use as the concentrate to mimic the operation of using ambient water as the concentrate. The effect of using an ambient concentrate increases the initial current draw to its maximum. This accelerates the process, but this high current throughout the process may be responsible for the decreased DOC recovery from tests with the same sample and Concentrate 1.

a higher salinity solution as the concentrate, the electrodialysis stack is initially much more conductive than when using a lower salinity concentrate. Thus, the current across the system was higher than in previous tests, and immediately reached the 1.5 A limit, and, because of the current limit placed on the power supply, required less voltage potential across the system than the 30 V limit. This is not apparent in Figure 4, as the low salinity concentrate resists ion movement, so the current draw is below the imposed limit and the full 30 V is applied. This higher current overall also caused the temperature of both solutions to increase (sample + 0.93 °C, concentrate + 1.7 °C) despite the ice bath. However, Tests 5 and 6 were notably faster than the previous tests; the total processing time was 23 minutes, compared to Tests 3 and 4, which lasted 32 minutes using the same sample and a lower salinity concentrate. Test 6 achieved 67% DOC recovery; the difference between it and the recoveries for Tests 3 and 4 may fall within the error bounds of calculating the DOC recovery or be a slightly lower recovery compared to those using a lower salinity concentrate because the higher current draw in Test 6 compared to Tests 3 and 4.

Complexity increases in high salinity solutions, in comparison to seawater. The first brine we tested was a NaCl-dominated brine taken from South Bay Salt Works (SBSW). SBSW is a salt-harvesting facility in Chula Vista, CA, in which water from the San Diego Bay has evaporated to create shallow ponds replete with NaCl and MgCl<sub>2</sub> salts (Roseman & Watry, 2008). These briny salt ponds have been proposed as analogs for future life detection missions (Klempay et al., 2021). Samples from Site 5 (MgCl<sub>2</sub>-saturated) and Site 11 (NaCl-saturated) of SBSW had been collected previously (Survey, 2011; Klempay et al., 2021), and were filtered to remove particles larger than 0.7 μm before test-



**Figure 6.** MR ED processing of 50 mL of a natural hypersaline solution, shows a less linear power increase throughout desalting as compared to the less saline solutions of ocean water from Skidaway River. Here, we show results for SBSW Site 11 sample. A low salinity (mixed to be 20 mS/cm conductivity)  $\text{Na}_3\text{PO}_4$  solution is used as the concentrate. In this experiment, the brine was successfully desalted to 0.91 mS/cm conductivity without precipitation – which is 0.8% its original salinity.

ing with the MR ED system. The SBSW Site 11 brine selected for use as Sample 3 is 1.86 times more concentrated in salt than compared to Earth’s seawater and was used in Tests 7 and 8. This brine was used to characterize the MR ED system’s ability to desalt a high salinity sample to 1 mS/cm conductivity, to establish such baselines as the time to desalt and power required, as well as to investigate the DOC recovery with more complex samples. Test 7 successfully desalted Sample 3 to the 1 mS/cm conductivity limit with a 77% DOC recovery, and the sensing data from this process is shown in Figure 6. Both salinity and power data are similar to those in Figure 5; the current is initially limited due to the high conductivity across the system, which is a result of using Concentrate 2, and the voltage increases in response to conductivity across the sample chamber decreasing. Concentrate 2 was a  $\text{Na}_3\text{PO}_4$  solution mixed to 20 mS/cm; the higher conductivity of the concentrate allowed for faster initial desalting. Test 7 was the longest test with a total processing time of 82 minutes, due to the high initial salinity of Sample 3. Additionally, we observed a decrease of 12 mL from the initial 50 mL sample volume, which stems from the osmosis of water molecules through the membranes (Jiang et al., 2015), and resulted in a concentration of the DOC in the sample and supported a higher DOC recovery.

In Test 8 we used Sample 3 as both the sample and concentrate in a manner similar to Test 5. Because both sample and concentrate were highly conductive (initial conductivity of 89.7 mS/cm), the current limit caused a much lower initial voltage (10.5 V) than in previous tests. After 50 minutes of desalting the conductivity of the sample stopped decreasing, and the experiment was terminated. The lowest conductivity that the sample reached was 48.2 mS/cm at which point 50% of the salts had been removed from the sample. When we disassembled the system for inspection, we observed precipitated salts

around the electrodes. Precipitate can cause clogging in fluidic channels and membranes, which can decrease the desalting efficiency as well as instigate reactions at the electrodes. Monitoring the sensing data during an experiment is important in order to observe potential issues such as precipitation.

In Tests 9 and 10 we tested Sample 4 to evaluate the MR ED system's performance with compositionally diverse brines. Mg brines in particular, such as Sample 4, may be of relevance to Europa (Zolotov & Shock, 2004). Sample 4 was prepared as an 8x dilution of SBSW Site 5 brine sample, and in Test 9 we prepared a concentrate of 1 L of Concentrate 1 (Table 1). While the conductivity of the sample decreased linearly for the 100-minute experiment, we noticed discrepancies in the current data. In Tests 2-4 that used Concentrate 1, the current was initially below the limit and steadily increased to the 1.5 A limit as the concentrate became more conductive. However, in the data from Test 9 the current started to decrease at 0.8 A, well below the limit. The low and decreasing current indicated low ion flow across the membranes, and the experiment was terminated. Although we did not observe precipitate around the electrodes that would explain the decreased ion flow due to clogging the membranes, the decreasing ion flow indicated that the process was unsuccessful. In Test 10 we used 500 mL of Sample 4 as the concentrate to improve the ion movement across membranes with a high salinity concentrate. This improved the ion flow, as the current draw was 1.5 A across the entirety of the test; however, we quickly noticed that the concentrate solution turned a pale-yellow color, and there was precipitation in the sample reservoir. Additionally, although the current data appeared as we would expect, the voltage initially decreased as the conductivity of the sample decreased, rather than increasing as in previous tests. The experiment ultimately stopped as a pump began to leak, and when the system was opened for inspection, salts had precipitated out of solution in the concentrate channels, particularly around the electrodes. The increased acidity of the sample and concentrate had corroded holes in the membranes, which were disposed of after the experiment. In Test 10 we recovered the sample solution to analyze the DOC recovery; the DOC recovery was 53% after the conductivity had decreased to 38% its initial value. These results indicate that a different procedure is required for highly saturated or acidic brines, such as lowering the current limit or applying a pulsed current to reduce the rate of ion transport and has been used to increase DOC recovery during late-stage ED when the desalting rate decreases (Gurtler et al., 2008).

## 4 Conclusions

The Miniature Robotic Electrodialysis system was designed for desalting small volumes of sample (less than 100 mL) as technology development for a liquid sample handling system for future ocean world missions for which proposed instruments would require desalting prior to analysis (Lawrence et al., 2021). However, such a small system has applications both on Mars and for field use Earth, allowing desalting of samples for many uses. We designed the MR ED system in order to increase the technology readiness level (TRL) of small-scale electrodialysis systems for desalting samples for the investigation of organics. Technology readiness levels provide an assessment of a particular technology's maturity with respect to spaceflight, from the observation of the basic principle (TRL1) to having been used successfully on a flown mission (TRL9) (Mai, 2015). After miniaturizing an ED system and successfully desalting natural samples containing primarily NaCl salts in a laboratory setting, we expect the technology readiness level of a milliliter-scale electrodialysis system to be elevated to TRL4, in which the technology has been validated in a laboratory environment. The extent of this work has validated the miniaturized, single cell-pair system for use on small volumes of Earth seawater and brines with NaCl salts. Further TRL elevation requires the system to be tested in a relevant environment to its planned use, as well as further developing the system to be used in-line with the organic-detecting instruments. For instance, to increase TRL

for use on Martian environments, the system should be tested with solutions containing perchlorates at the expected concentration.

The design of MR ED has a low complexity and ease of configuration. The system can be reliably opened for inspection and reassembled, and the separate chambers that comprise the assembly can be either machined or 3D printed from resin, making it easily replicable. These channels of fluid, which are thicker than cells in commercial ED stacks, allow greater mixing of the fluid that enables a higher DOC recovery as well as enhances the efficiency. Experimentation and sensing illuminated us to certain components of the design, such as temperature management. The inclusion of the ice bath for sample and concentrate containers was introduced after tests showed large temperature increases. As the temperature of both the sample and concentrate affect their conductivity, a colder sample and concentrate will be slightly more insulative than a warmer sample and concentrate. This prevents excess current from conducting through the system, and could lead to a larger recovery of DOC. Thus, temperature management for this system will be important in the design in an instrument package; this would additionally benefit downstream instruments by keeping the sample at close to its natural state. A similar aspect of the design was the in-line power sensing, which allowed us a greater understanding of the process that was sealed inside the system. Monitoring the power, and understanding the nominal operation of the power system, allowed us to see that the desalting efficiency was reduced due to precipitated salts in several tests. Future development plans include developing the autonomy by using the Raspberry Pi to control the pumps and the voltage and current limits of a power system according to conductivity and temperature readings of the sample. This all should be contained to a waterproof housing to allow in situ testing and field deployments.

Processing with electrodialysis is a destructive technique; however, we have shown that a significant amount of dissolved organic carbon can be recovered. The issues salts pose to instruments that detect organic signatures are great, thus we conclude that a destructive technique is useful to remove destructive elements of the sample while retaining measurable components. In our tests, the MR ED system, processing less than 10% of the volume of sample processed by established instruments, achieved successful desalting of natural samples and NaCl brines to a conductivity of 1 mS/cm with DOC recovery spanning a range from 53% to 77%, which is comparable to desalting with established laboratory electrodialysis systems that recover on average 70% DOC (Chambers et al., 2016; Gurtler et al., 2008; Koprivnjak et al., 2006; Vetter et al., 2007). Best recovery was achieved after optimizing the experimental set up, where MR ED successfully desalted NaCl brines using a low salinity Na<sub>3</sub>PO<sub>4</sub> concentrate and retained 77% DOC after removing 99.2% the salts. However, tests with brines containing MgCl<sub>2</sub> salts resulted in salt precipitated out of solution and further investigation is needed to optimize desalting brines. Potential measures that could be used to improve operation with brines include processing with a different composition concentrate, processing at a lower power draw or with a pulsed current, or circulation at a different flow rate. Finally, we showed that MR ED achieved 67% DOC recovery when using a separate stock of the initial natural sample as the concentrate, thus operating as an in situ system would by using surrounding water as the concentrate. This is a unique operation that has not yet been tested on established systems. These experiments establish the utility and baseline capabilities of an autonomous miniature electrodialysis system to be used with an instrument package in high salinity environments.

## 5 Open Research

The sensing data, measurement data, and observations used for analysis of the electrodialysis efficiency and effectiveness in this study are available at Zenodo, Github via <https://zenodo.org/record/7076436> under the Creative Commons Attribution 4.0 International license (Bryson et al., 2022). A persistent link to the Jupyter notebook used

for data collection and observations is available at [https://mybinder.org/v2/gh/fbryson820/Development-of-MRED-Data.git/main?labpath=Development%20of%20the%20Miniature%20Robotic%20Electrodialysis%20\(MR%20ED\)%20System%20for%20Small-Scale%20Desalting%20of%20Liquid%20Samples%20with%20Recovery%20of%20Organics.ipynb](https://mybinder.org/v2/gh/fbryson820/Development-of-MRED-Data.git/main?labpath=Development%20of%20the%20Miniature%20Robotic%20Electrodialysis%20(MR%20ED)%20System%20for%20Small-Scale%20Desalting%20of%20Liquid%20Samples%20with%20Recovery%20of%20Organics.ipynb)

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