SNO-STR-95-021

MONITORING OF LIGHT AND HEAVY WATER SYSTEMS IN SNO FOR PARAMETERS OTHER THAN RADIOACTIVITY

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Isotopic D_2O/H_2O. Dentate MnO_2 beads

Dm H_2O

H in D_2O.

Introduction

The water used in the SNO experiment must be very low in radioactivity (10^{-15} g/g Th and U for D_2O and 10^{-14} g/g Th and U in H_20) and possess good optical clarity. Techniques have been developed to monitor the radioactivity and evaluate optical clarity. However, there must be monitoring of the water system itself in order to assess cleanliness (other than radioactivity) and integrity of these systems. A monitoring scheme for the light and heavy water systems in the SNO experiment should be devised in order to observe critical parameters that give trend information and provide an alarm when the steady state is upset.

Impurities such as dissolved solids, organics, silica, particles, and bacteria exit in even the purest of water. As a result, users of high purity water have put limits on these contaminants. For example, the semiconductor industry has several guidelines for water quality requirements. Although SNO has a unique application for high purity water, it is thought that the stringent guidelines adopted by the semiconductor industry are a good example to follow. There are several options available for monitoring various parameters. This document outlines ideal parameter guidelines, some of which the limits still have to be established for our application, and explores options for monitoring of these parameters.

Semiconductor Industry Standards

Parameter	E-1ASTM[1]	SEMI1985[2]	Balazs[3]	Japan[4]
Resistivity, megohms-cm at 25degree C	18*	17.9*	18.2	17.5
Bacteria/mL	1	6/100mL	0.1/100mL	0.01
Particles (>1um)	2/mL	1/mL	1/L	
(>0.05um)				20/mL
TOC,ppb	50	50	10	50
Silica (as SiO2)ppb	5	5	0.5	5
K	2ppb	0.3ppb	0.02ppb	
Mn		0.5ppb	0.004ppb	
Ni			0.005ppb	
Fe		0.1ppb	0.01ppb	

1- American Society for Testing and Materials (E-1 is the highest grade water)
2-Semiconductor Equipment and Materials Institute - guidelines developed in conjunction with Balazs Analytical Laboratories
3-Balazs 1993 Attainable Guidelines

4- Japan Electronic Specifications
* 18 megohm-cm, 90% of the time, with a 17 Megohm-cm minimum at 25 degree C

What We Should Measure and Why

In addition to the standard on-line monitoring of the water system which is already in place (hardness (H_2O system), pH, temperature, resistivity, and pressure) it is recommended that more specific contaminants be measured. While resistivity, which detects ionic impurities, provides some diagnostic information it does not provide specific information on a number of other potential impurities. These include TOC, bacteria, particle counts, silica, dissolved oxygen and specific anions/cations/metals such as sulfate, potassium, manganese, nickel, iron or titanium.

TOC (total organic carbon) is a nutrient for bacteria and could be indicative of leaching or shedding from components such as pipes, storage tanks, acrylic vessel, MnO_2 beads, and RO or UF membranes. TOC may also be an indicator of microbial presence. Because TOC does not differentiate between bacteria and other organic matter it is useful to also have a bacterial analysis. Undetected microbial growth and development of biofilm can affect optical clarity and cause biofouling of components. Particle counts which include colloids, bacteria, metal oxides, silicates, and organic matter is a useful measurement since colloids and metal oxides are not detected by the other methods. Since it includes a number of parameters in one analysis it is a good regular monitoring tool. Particles can be generated from a number of steps in the water purification process (ie shedding of filters, membranes and resins or formation of metal oxides and colloids due to presence of metals) or may have simply been present in the feed water and have escaped through the filtering system. Dissolved oxygen is an important parameter to monitor since it can be a nutrient source for bacterial growth and a catalyst for corrosion, as well as an indicator for poor "air tightness" of the system. It is assumed that both water systems are to be operated in an deoxygenated mode. K is of interest to SNO because of K^{40} radioactitvy. Also of interest, because of leaching from MnO_2 beads, is manganese. Elevated concentrations of Mn may indicate problem with the beads. The presence of metals in general may interfere with other analysis such as SUF. Because of the presence of mine dust, it may be useful to look for silica and sulfur (ie in the form of sulfate). Ni may reflect leaching from hastelloy/NC detectors and Fe may point to leaching from stainless steel components. Is shedding of Ti from HTiO a potential problem?

Type of Analysis - On-line or Off-line

From the above, the parameters that should be measured on-line include resistivity and dissolved oxygen. It is generally recommended that particle counts be done on-line but it can be done off-line if our requirements are not too stringent. Any measurement that is done off-line

is not as sensitive because of higher background interferences. One reason for performing off-line analysis is that we would not have to purchase our own equipment - the samples could be sent to an outside laboratory. On-line equipment has to be very carefully chosen since any component that the water comes in contact with could potentially impart radioactive contamination. Furthermore, the operation of an in-house instrument requires a dedicated clean area and a dedicated person operating and maintaining it.

Options for Monitoring of Various Parameters

The following is a breakdown of available instruments and analyses. All prices except for those associated with Accutest Laboratories are quoted in U.S. dollars. All prices quoted for Analytical Services Inc do not include shipping and handling.

TOC

Outside Analysis

So far, one company that specializes in ultrapure water analysis, Analytical Services Inc located in Essex Junction, Vermont, has been contacted .

Cost	$70
Sample Size	250 mL
MDL	1ppb
Sample integrity	they provide specially prepared bottles; some volatiles will be lost due to handling; sampling must be done very carefully in the absence of solvents, etc.

Total cost for duration of experiment:

once a day for 5 years:	$127,750(at 250mL/smple this represents approx 300L D_20)*
Once a week for 5 years:	$ 18,200
Once a month for 5 years:	$ 4,200
Once a day for 10 years:	$255,500
Once a week for 10 years:	$ 36,400
Once a month for 10 years:	$ 8,400

*An inquiry into either retrieving the left over sample, modifying the analysis or using another type of instrument (in order to use less sample) still has to be made.

Purchase of Instrument:

Company	Anatel
cost	$17,200
MDL	25ppb
Sample Size	7 mL
Mode	designed as on-line, can be used off-line
Recovery of sample	sample is exposed to phosphoric acid and sodium persulfate, so it can either be disposed of or retained for later cleanup

Company	O-I Corporation
Cost	$17,865
MDL	2-6 ppb
sample size	10 mL
Mode	designed as off-line, could be modified for on-line
recovery of sample	same as above
on-line use	pressurized water sample enters sample loop - main water stream not exposed to instrument components

Particle Counting

The three most common methods used for particle counting in the high purity water business are SEM (scanning electron microscope), epifluorescence and laser particle counting. Epifluorescence is designed for bacteria counting but SEM and laser counting are potential candidates.

SEM (outside analysis)

Analytical Services provides a grab sampling option for particle and bacteria enumeration by Scanning Electron Microscopy. Samples are collected by filtering a sample stream through a 25 mm track-etch polycarbonate membrane in specially prepared holders. The standard pore size of the membranes are either 0.08 um or 0.2um but other pore sizes are available. See appendix for more information. The company will send the filter to us, we do the sampling, then send it back to them for analysis.

Sample size	depends on accuracy and detection limits required - for example: 500 L is required for good statistical analysis of very clean water
Cost	$200
MDL	0.05um
Advantage	bacteria (dead and alive) and particles are differentiated
recovery of water	water run through filter can be directed toward a storage tank and if necessary can be cleaned later

Total cost	
once a day for 5 years:	$365,000
once a week for 5 years:	$ 52,000
once a month for 5 years:	$ 12,000
once a day for 10 years:	$730,000
once a week for 10 years:	$104,000
once a month for 10 years:	$ 24,000

Laser Particle Counter

Company	Horiba
Model	PLCA-311, on-line
cost	$34,250
sample rate	60ml/min or 260ml/min
Sensitivity	0.085um or 0.1um depending on sample rate
wetted parts	sapphire and teflon

Company	Horiba
model	PLCA-700,off-line or on-line
cost(off-line)	$46,500
sample size	1000ml
sensitivity	0.1um
wetted parts	sapphire, teflon

Bacteria

Outside Analysis - Analytical Services

Method 1	Epifluorescence, sample filtered on a loaded filter provided by the company
cost	$40

Total cost	
once a day for 5 years:	$ 73,000
Once a week for 5 years:	$ 10,400
once a month for 5 years:	$ 2,400
once a day for 10 years:	$146,000
once a week for 10 years:	$ 20,800
once a month for 10 years:	$ 4,800

Method 2	SEM, included as part of particle counting

Epifluorescence

Cost of a microscope and fluorescence attachment are available from companies such as Nikon and Olympus and cost about 10,000 dollars. In addition to this one would need to purchase a sampling unit and filters for obtaining the water sample. This cost has not yet been determined.

Anion/Cation Analysis (Outside Analysis)

Analytical Services

Parameters	Fluoride, chloride, phosphate, bromide, nitrate, sulfate, sodium, ammonium, potassium
Cost	$150
sample size	250 mL
Method	ion chromatograph
MDL	50 ppt

Note:
The cost is $150 even if one parameter is measured.

Accutest Laboratories, Ottawa

Parameter	Potassium	Sulfate
Cost	$7	$12
Sample size	30mL	
MDL	10 - 50 ppb	0.5 - 1 ppm

Trace Metals

Company	Analytical Services
Parameters	See appendix
Method	iron, silicon, calcium by ICP/AES, all others by ICP/MS
MDL	iron- 0.2ppb
	Si - 1ppb
	Ti - 0.1ppb
	Ni - 80ppt
	Mn - 60ppt

Nonvolatile Residue

The semiconductor industry recently introduced nonvolatile residue as a parameter in the set of ASTM guidelines at a limit of 1 ppb. In this type of analysis a sample of water is evaporated and the remaining residue is weighed. The contaminants that make up this residue consist of dissolved inorganics, colloidal silica, organics, particles and bacteria. Particles and bacteria represent very little of the weight; the predominant fraction is dissolved inorganics.

Company	American Fluid Technologies
MDL	10ppb
sample size	50ul
cost	$43,500 base model U.S.
	$51,000 on-line/off-line capabilities
wetted components	teflon, sapphire, passivated 316 stainless steel

Final Comments

All of the above represent a significant cost. If "outside" analysis is opted for, it is proposed to investigate at least one more company for prices and limits of detection. As well, frequency of desired analysis needs to be determined. As to in-house instrumentation, we have not mentioned the possibility of purchasing an ion/metal analyzer. This again is associated with at least a $50,000 expense.

In general, in-house analysis seems to be the more expensive option and unless otherwise recommended, we would proceed to check further into the "outside" analysis option. Using the "outside" analysis option also means that no further provision in the design of the water systems have to me made since sampling ports have already been accounted for.

Analytical Services, Inc.

P.O. Box 626
Essex Junction, VT 05453

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Toll Free: (800) 723-4432
Fax: (802) 878-6765

February 6, 1995

Ms. Cathy Shewchuk
Carleton University
Dept. CRPP
Ottawa, Ontario, Canada KIS5B6

VIA FAX: 613-786-7546

Dear Cathy:

I hope you find this material informative. The parameters included in our Ion Chromatography analysis are given in the lower right corner box of the trace ion sheet. The cost for this service is $150.00 per sample. The cost of analysis of the entire page is $550.00 per sample.

The cost of SEM particle and bacteria counting is $200.00 per sample. Particle analysis is available for an additional $175.00 per twenty particles.

Quantity discounts are available. All above figures expressed as US dollars.

Please call me if you have any questions, or if you wish to place an order.

Sincerely,

ANALYTICAL SERVICES, INC.

Thomas M. Hargy
Ultrapure Water Services Manager

Analytical Services, Inc.

ULTRAPURE WATER

Standard Detection Limits for Trace Ion Analysis

Parameter	Detection Limit	Parameter	Detection Limit	Parameter	Detection Limit
Aluminum	0.10 µg/L	Iron*	0.20 µg/L	Tantalum	0.08 µg/L
Antimony	0.08 µg/L	Lanthanum	0.05 µg/L	Tellurium	0.25 µg/L
Arsenic	0.03 µg/L	Lead	0.07 µg/L	Terbium	0.10 µg/L
Barium	0.08 µg/L	Lithium	0.30 µg/L	Thallium	0.08 µg/L
Beryllium	0.05 µg/L	Lutetium	0.05 µg/L	Thorium	0.03 µg/L
Bismuth	0.15 µg/L	Magnesium	0.07 µg/L	Thulium	0.04 µg/L
Boron	0.20 µg/L	Manganese	0.06 µg/L	Tin	0.25 µg/L
Cadmium	0.08 µg/L	Mercury	0.01 µg/L	Titanium	0.10 µg/L
Calcium*	0.05 µg/L	Molybdenum	0.02 µg/L	Tungsten	0.02 µg/L
Cerium	0.04 µg/L	Neodymium	0.09 µg/L	Uranium	0.03 µg/L
Cesium	0.08 µg/L	Nickel	0.08 µg/L	Vanadium	0.11 µg/L
Chromium	0.26 µg/L	Niobium	0.03 µg/L	Ytterbium	0.04 µg/L
Cobalt	0.10 µg/L	Palladium	0.10 µg/L	Yttrium	0.03 µg/L
Copper	0.08 µg/L	Platinum	0.13 µg/L	Zinc	0.05 µg/L
Dysprosium	0.01 µg/L	Praseodymium	0.10 µg/L	Zirconium	0.11 µg/L
Erbium	0.05 µg/L	Rhenium	0.10 µg/L	Anions/Cations	
Europium	0.03 µg/L	Rhodium	0.10 µg/L	Fluoride	0.05 µg/L
Gadolinium	0.05 µg/L	Rubidium	0.01 µg/L	Chloride	0.05 µg/L
Gallium	0.40 µg/L	Ruthenium	0.12 µg/L	Phosphate	0.05 µg/L
Germanium	0.03 µg/L	Samarium	0.06 µg/L	Bromide	0.05 µg/L
Gold	0.03 µg/L	Scandium	0.10 µg/L	Nitrate	0.05 µg/L
Hafnium	0.10 µg/L	Selenium	0.50 µg/L	Sulfate	0.05 µg/L
Holmium	0.10 µg/L	Silicon*	1.0 µg/L	Sodium	0.05 µg/L
Indium	0.07 µg/L	Silver	0.03 µg/L	Ammonium	0.05 µg/L
Iridium	0.02 µg/L	Strontium	0.10 µg/L	Potassium	0.05 µg/L

*Analysis by ICP/AES. All other metals by ICP/MS. Anions/cations by IC.

Analytical Services, Inc.

PARTIAL LISTING OF ANALYTICAL SERVICES INC. ULTRAPURE WATER DIVISION'S CLIENTS

Bell Northern Research, Ottawa, Ontario
Bio-Lab, Inc., Dorval Quebec, Canada
Boehringer, Ingelheim Pharmaceuticals, Inc., Danbury, CT
C. B. Strain & Son, Inc., Poughkeepsie, NY
Carten Controls, Middlebury, CT
Champlain Water District - So. Burlington, VT
COSTAR Corp. - Kennebunk, ME
Culligan Water Conditioning, Inc., Bethel, CT
Fluoroware Corp. - Chaska, MN
Fresenius AG. - Wendel, Germany
High Purity Technology, Inc. - Poughkeepsie, NY
HSI Water Treatment, Hillsboro NC
IBM Corp. - Bromont, Quebec
IBM Corp. - East Fishkill, NY
IBM Corp. - Essex Junction, VT
IBM Corp. - Mainz, Germany
IBM Corp. - Manassas, VA
Intel Corp. - Rio Rancho, NM
Integrated Gas Systems, Inc., Fishkill, NY
Ionpure Technologies, Inc., Lowell, MA
Kinetic Systems, Inc., New Berlinville, PA
MEMC Microelectronics, Inc., St. Peters, MO,
MEMC Microelectronics, Inc., Spartanburg, SC
Memtec America Corporation, Timonium, MD
Metcalf & Eddy, Tampa, FL
MITEL Corp., Bromont, Quebec
Pall Corporation, East Hills, NY
Parker Hannifin Filter Division, Lebanon, IN
Polymetrics, Inc. - So. Windsor, CT
Quasar Engineering, Inc., Santa Clara, CA
Raytheon Co., Andover, MA
Schutz Container Corp. - North Branch, NJ
Sverdrup Corporation, St. Louis, MO
PTI-Textron Corporation, Newbury Park, CA
The Texwipe Company, Kernersville, NC
Ulshafer Associates, Inc. - Colchester, VT
Ultravatten, (Asea Brown Boveri) Sweden
Whiting-Turner Co., Baltimore, MD

Analytical Services, Inc.

Ultrapure Water

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Analytical Services, Inc. (formerly I.E.A.) combines years of experience with advanced instrumentation to deliver accurate and precise analytical results. Analyses include routine performance monitoring and special pilot and research projects. Results from Analytical Services, Inc. enable you to know whether you are meeting your ultrapure water specifications.

Field Services

We get the scientists and the equipment to your site to perform a variety of services:

- Provide on-site instruments for monitoring the quality of ultrapure water systems
- Collect samples at customer locations for lab analysis
- Install and maintain Point of Use filters
- Provide assistance in system start-up and trouble-shooting
- Provide long term maintenance services for ultrapure water systems
- Set up our ozone generator for quick, economical, chemical free sanitization

Microbiological

- Bacterial enumeration by the Scanning Electron Microscopy (SEM) Direct Count Method
- Bacterial enumeration by epifluorescence procedures
- Bacterial counts utilizing APHA, ASTM or specifically designed procedures
- Bacterial identification by Fatty Acid Profile
- Biofilm Monitoring
- Endotoxin analysis by Limulus Amebocyte Lysate (LAL) assay

Particulate

- Particle sizing and enumeration by the SEM Direct Count Method
- Elemental analysis of particles by Energy Dispersive Spectroscopy (EDS)
- On-line particle counts by laser analyzer sensitive to the .05μm size range

Chemical

- Trace ion analysis to the sub parts per billion (ppb) range utilizing ICP/MS, ICP/AES and ion chromatography (IC)
- Total Organic Carbon (TOC) on-line analysis to the ppb range
- Material composition analysis by SEM/EDS

Product Testing and Research

Analytical Services designed and constructed its own in-house ultrapure water system using state-of-the-art equipment and instrumentation. This 20 gpm recirculating facility enables us to provide independent laboratory testing of any ultrapure water system component. Our product services assist end-user decision making for component purchases and provide manufacturers with validation for new products and designs. Tests include:

- Rinse down rate of resins and filters to background quality levels
- Filter efficiency
- Filter shedding analysis
- Leaching test
- SEM inspection
- Purity testing of piping materials and valves

Put us to the Purity Test

Contact Analytical Services and discover how years of experience, a dedicated staff, and advanced instrumentation combine to provide you with the highest quality services available for ultrapure water systems.

Analytical Services, Inc.

Particle and Bacteria Enumeration by Scanning Electron Microscopy (SEM)

The efficient operation of any ultrapure water system depends heavily on accurate performance evaluation. Monitoring particle and bacteria levels throughout a system is one important parameter in this assessment. The SEM technique allows economical particle enumeration of water samples collected from any sampling point on a system. By using multiple sampling rigs, data from multiple sites can be gathered simultaneously. Unlike laser particle counting techniques, particles and bacteria can be differentiated. In the past 10 years, Analytical Services has analyzed over 14,000 ultrapure water samples using this methodology.

Samples are collected by filtering a sample stream through 25mm track-etch polycarbonate membrane filters held in specially prepared holders. The standard pore size of the membranes are either 0.08μm or 0.2μm. Other pore sizes are available. Background particle levels of each collection filter is determined prior to use.

Following collection, the filters are returned to our laboratory where they are prepared in a Class 100 clean hood. Preparation involves mounting the sample filter on a conductive planchet, drying, and sputter coating with 180Å of gold, to facilitate electron conductivity.

Analysis is performed with a JEOL 840A Scanning Electron Microscope, which allows resolution of particles of 0.05μm diameter. For samples of ultrapure water, 400 random fields are examined. Particles are counted and categorized by size, and total bacteria are also counted. Following the count, the average count per field for each size category is calculated, and counts per Liter of sample filtered are determined, with a 95% confidence interval given.

An additional value of SEM technology is the capability to characterize the composition of materials. Using Energy Dispersive Spectroscopy (EDS), the SEM technique makes elemental identification of even sub-micron particles possible. This information can be used to identify the source of contamination.

As with any ultrapure water analysis, careful sampling procedure is very important. Analytical Services, Inc.'s field staff is available to design and set up appropriate sampling sites and carry out the collection. Alternatively, materials and instructions can be provided to the client with our **SEM EXPRESS** service to enable in-house collection of particle samples.

For more information, please call our Ultrapure Water division at 800-723-4432.

- run about 500L
- good to run high volume to get good statistical analysis
- for D_2O system water should run to storage tank. In which case the assembly should be tested for Rn emanation