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Ion Exchange Filter Transition Plan for BWRs and PWRs

3002000371

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Technical Update, March 2013

EPRI Project Manager

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ACKNOWLEDGMENTS

The following organization, under contract to the Electric Power Research Institute (EPRI), prepared this report:

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This report describes research sponsored by EPRI.

EPRI thanks chemistry personnel at the BWR and PWR stations and ion exchange membrane vendors for participating in an industrywide survey and providing data that are included in this report.

This publication is a corporate document that should be cited in the literature in the following manner:

Ion Exchange Filter Transition Plan for BWRs and PWRs. EPRI, Palo Alto, CA: 2013. 3002000371.

PRODUCT DESCRIPTION

This report includes an interim review of plant experiences with various cation exchange membranes to determine if new filters are comparable and suitable for nuclear power plant chemistry applications. Gaps in performance and impacts to recommendations in EPRI reports *BWRVIP-190: BWR Vessel and Internals Project, BWR Water Chemistry Guidelines - 2008 Revision (1016579), Pressurized Water Reactor Primary Water Chemistry Guidelines (1014986)* and *Pressurized Water Reactor Secondary Chemistry Guidelines – Revision 7 (1016555)* are identified.

Background

Analysis and quantification of reactor water, feedwater, and chemical and volume control system (CVCS) soluble metals radioisotopes are essential for monitoring species that impact fuel performance, steam generator and heat exchanger performance, mitigation of stress corrosion cracking of reactor piping and internals, and radiation fields and for ensuring that dose mitigation techniques are effective. Soluble species in the CVCS, feedwater, reactor water, and other process sample streams are usually collected on ion exchange membranes after the sample has passed through a 0.45 or 0.1 μm membrane filter. Cationic species are predominantly of interest. Most nuclear plants currently use cation exchange membranes from Toray Industries, Inc.

In September 2012, it was reported that Toray Industries, Inc. would discontinue the manufacturing of cation exchange membranes at the end of 2012.

Objectives

- To evaluate plant experiences with commercially available cation exchange membranes to determine viable options for nuclear power plant chemistry applications
- To provide guidance on how plants can transition to use of ion exchange membranes from new vendors

Approach

The majority of the information presented is based on responses to an industry survey issued in 2012. Additional information was obtained from ion exchange membrane vendors.

Results

Based on available plant experience, one of the most common differences observed when comparing the performance of ion exchange membranes from different vendors was recovery amounts. As was seen at the Cooper and Dresden plants, the difference in recovery amounts can be significant. In most cases, recovery was lower with Graver membranes than with membranes from Toray Industries, Inc. Additional analysis is required to understand why both plants saw low recovery for various metals.

Additional plant data are required in order to perform statistical analyses of the performance of ion exchange membranes from different vendors. To determine if ion exchange membranes perform comparably in a given laboratory method, multiple ion exchange membranes should be analyzed in a similar matrix so that statistically significant testing can be performed.

The Monticello and Vattenfall plants also documented issues with high blank contamination on ion exchange membranes. Monticello had historically measured blank contamination of less than 1 µg for metals, but has seen higher than expected amounts of nickel and zinc on cation exchange membranes, with and without rinsing. Monticello has provided information to the vendor for resolution.

Consideration should be given to the development of a qualification program to be performed by an independent laboratory that would encompass tests on the characteristics of various ion exchange membranes. Tests could include recovery efficiency, capacity determination, thickness, metallic impurities, resin dispersion, etc. Test conditions such as sample volumes, sample temperature, and filtration flow rate would be specified and reported. Methodologies for acceptable digestion of ion exchange filters for use with atomic absorption spectroscopy or inductively coupled plasma analyses would be determined. The suitability of each ion exchange membrane for analysis by X-ray fluorescence would also be determined.

Applications, Value, and Use

This interim report is intended for use by BWR and PWR chemistry personnel to assist with the transition to a new ion exchange membrane. Information presented in this report will be used in future work to close identified gaps, including additional testing and analysis of filter performance.

Keywords

BWR
Cation
Chemistry
Ion exchange
PWR
Soluble

ABSTRACT

This report includes an interim review of plant experiences with various cation exchange membranes to determine if new filters are comparable and suitable for nuclear power plant chemistry applications. Gaps in performance and impacts to recommendations in EPRI reports *BWRVIP-190: BWR Vessel and Internals Project, BWR Water Chemistry Guidelines - 2008 Revision (1016579), Pressurized Water Reactor Primary Water Chemistry Guidelines (1014986)* and *Pressurized Water Reactor Secondary Chemistry Guidelines – Revision 7 (1016555)* were identified by evaluating plant experiences and compiling the results from a 2012 industry survey on commercially available cation exchange membranes.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION

Analysis and quantification of reactor water, feedwater, and chemical and volume control system (CVCS) soluble metals radioisotopes are essential for monitoring species that impact fuel performance, steam generator and heat exchanger performance, mitigation of stress corrosion cracking of reactor piping and internals, radiation fields and ensuring that dose mitigation techniques are effective. Soluble species in the CVCS, feedwater, reactor water and other process sample streams are usually collected on ion exchange membranes after the sample has passed through a 0.45 or 0.1 µm membrane filter. Cationic species are predominantly of interest. Most nuclear plants currently use cation exchange membranes from Toray Industries, Inc.

In September 2012, it was reported that Toray Industries, Inc. would discontinue the manufacturing of cation exchange membranes at the end of 2012. Similar reports were received concerning Pall ion exchange membranes. These reports prompted many plants and utilities to begin looking at other products from various vendors to replace their current ion exchange membranes.

With this possible change having a potential impact on the water chemistry analyses that are important for monitoring fuel reliability, corrosion and dose control established in the Boiling Water Reactor (BWR) Water Chemistry Guidelines [1], Pressurized Water Reactor (PWR) Primary Water Chemistry Guidelines [2] and PWR Secondary Water Chemistry Guidelines [3], an interim evaluation of ion exchange membrane availability from various vendors and plant experiences was conducted.

This report includes an interim review of plant experiences with various cation exchange membranes to determine if new filters are comparable and suitable for nuclear power plant chemistry applications. Gaps in performance and impacts to recommendations in BWR Water Chemistry Guidelines [1] and PWR Primary and Secondary Water Chemistry Guidelines [2, 3] are identified.

The majority of the information presented is based on responses to an industry survey issued in 2012. Additional information was obtained from ion exchange membrane vendors. Information presented in this report will be used in future work to resolve identified gaps towards a successful transition to new ion exchange membranes as changes are required or desired by stations. This report is not intended to identify a preferred vendor, but to provide experiences with ion exchange membranes from different vendors and to provide considerations and recommendations to plants requiring or desiring a change.

2

BACKGROUND AND INDUSTRY GUIDANCE

Sampling and analysis for activated and non-activated corrosion products and other metals in the reactor water, feedwater, condensate and chemical and volume control system (CVCS) provides plant chemistry personnel with relevant information associated with maintaining fuel integrity, monitoring corrosion and controlling radiation fields. Grab sampling and integrated sampling methods are utilized in BWRs and PWRs. In some cases, such as feedwater sampling, integrated sampling devices are required as large volumes of system water must pass through the filters to concentrate the species of interest in order to meet lower detection limits of laboratory instrumentation.

With each method, samples are first passed through a 0.45 or 0.1 μm membrane to remove filterable species. Membrane filters are typically cellulose esters and have no ion exchange capacity. After passing through the membrane, colloidal and soluble species are removed by ion exchange membranes. All plants utilize cation ion exchange membranes for soluble iron, nickel and copper sample collection. Cation exchange membranes are also used to collect soluble zinc in feedwater and, in many cases, in reactor water also. Some also use anion ion exchange membranes to capture anionic species, such as chromate. The filters are then analyzed using atomic absorption spectroscopy or inductively coupled plasma following acid digestion or filter elution or directly (no digestion) using X-ray fluorescence.

When atomic absorption spectroscopy or inductively couple plasma instruments are utilized, ion exchange membranes must be digested or eluted prior to analysis. With acid digestion, most plants utilize concentrated nitric acid to dissolve the filters in a microwave digester. After a cooling period, the volume of the digested filter and acid is typically diluted to a known volume. In the elution process, a combination of hydrochloric and nitric acids are used to rinse the charged species from the filters, allowing the filters to be re-used in some cases. This process is similar to an ion chromatography column where a more highly charged species replaces the species of interest from the stationary phase.

Ion exchange membranes were originally supplied as filter papers coated with powdered ion exchange resins. While this application was relatively inexpensive, the consistency of the powdered resin coating was an issue. These membranes had low capacities for ion exchange. Gelman SA 6404 cation ion exchange membranes, which were among the first ion exchange filter media used in nuclear plant applications, consisted of filter paper with powdered ion exchange resin impregnated into the surface. The desirable membrane characteristics reported in 1990 included capacities greater than 0.05 meq (milli-equavalents) per membrane, metallic impurities less than 4 μg per membrane and for the membranes to have "no holes" evident [4]. Due to low capacity of these membranes, multiple membranes were stacked in the filter housing. The stack typically included a 0.45 or 0.1 μm membrane, followed by 2 or 3 cation ion exchange membranes and then 2 anion ion exchange membranes.

Much like the current issue involving the major suppliers discontinuing production of cation ion exchange membranes, Gelman discontinued the SA 6404 ion exchange membranes in late 1989, requiring plants to find alternate products for collection of soluble ionic impurities, particularly metals. In response, GE Nuclear Energy evaluated multiple ion exchange membranes, examining them for several different characteristics. Filter thickness, resin particle size, shape and dispersion and capacities of multiple membranes were reviewed to determine membranes to be used for in-plant testing [4]. Capacities and metallic impurity results from these 1990 tests are shown in Tables 2-1 and 2-2.

Table 2-1
GE Nuclear Cation Ion Exchange Static Capacity Test Results [4]

Cation Exchange Membrane Manufacturer/Part Number	Vendor Quoted Capacity Value (meq/membrane)	Lab Measured Capacity Analysis (meq/membrane)
Gelman SA-6404	0.05	0.034 – 0.055
Gelman SA-6404	0.05	0.011 – 0.037
Gelman SA-3S	----	0.018 – 0.022
Gelman SA-3T	----	0.013 – 0.018
Toray	0.83	0.62 – 0.70
Bio-Rad	2.63	2.05 – 2.26
Cuno	----	0.001 – 0.063

Table 2-2
GE Nuclear Cation Ion Exchange Membrane Metallic Impurities Test Results [4]

Manufacturer	Impurity Amount (μg/membrane)						
	Zn	Mn	Fe	Ni	Cu	Co	Cr
Bio-Rad	0.2	0.1	5.0	0.3	0.1	0.1	0.6
Toray	1.3	0.1	2.3	0.1	0.1	0.1	0.6
Gelman SA 6404	1.3	0.6	4.3	0.1	0.2	0.1	0.6
Gelman SA-3T	0.7	14.0	3.3	0.1	2.0	0.1	0.6
Gelman SA-3S	1.0	0.1	5.3	0.1	0.2	0.1	0.6

During this time period, cellulose fibers were first seen in ion exchange membrane applications. Toray Industries, Inc. developed a cation ion exchange membrane, CP-1, composed of cellulose fibers with long fibrous resins [4]. Polystyrene fibers were imbedded in a polyethylene matrix with the polystyrene functionalized with anion or cation exchange sites.

The application use of fibers in the ion exchange membranes is based on filter demineralizer precoat useage. Cellulose fibers were used to improve flow characteristics and reduce differential pressure across a precoat surface. When used with charged materials such as ion exchange resins, the charged fibers improved the removal of soluble materials [5].

Use of Toray filters became widespread in the late 1990s, remaining the ion exchange membrane of choice until the recent focus on transition. As shown in Figure 2-1, 24 of the 30 responses received during a 2012 industry survey concerning use of cation ion exchange membranes indicated use of the Toray CP-1 cation ion exchange membranes. In late 2012, information was exchanged stating that the major suppliers of cation ion exchange membranes, Toray Industries, Inc. and Pall, would discontinue production of ion exchange membranes currently used in nuclear power plant chemistry sampling applications, prompting evaluations by plants and utilities for alternative membranes and evaluation of the associated impacts on chemistry analyses important to process monitoring.

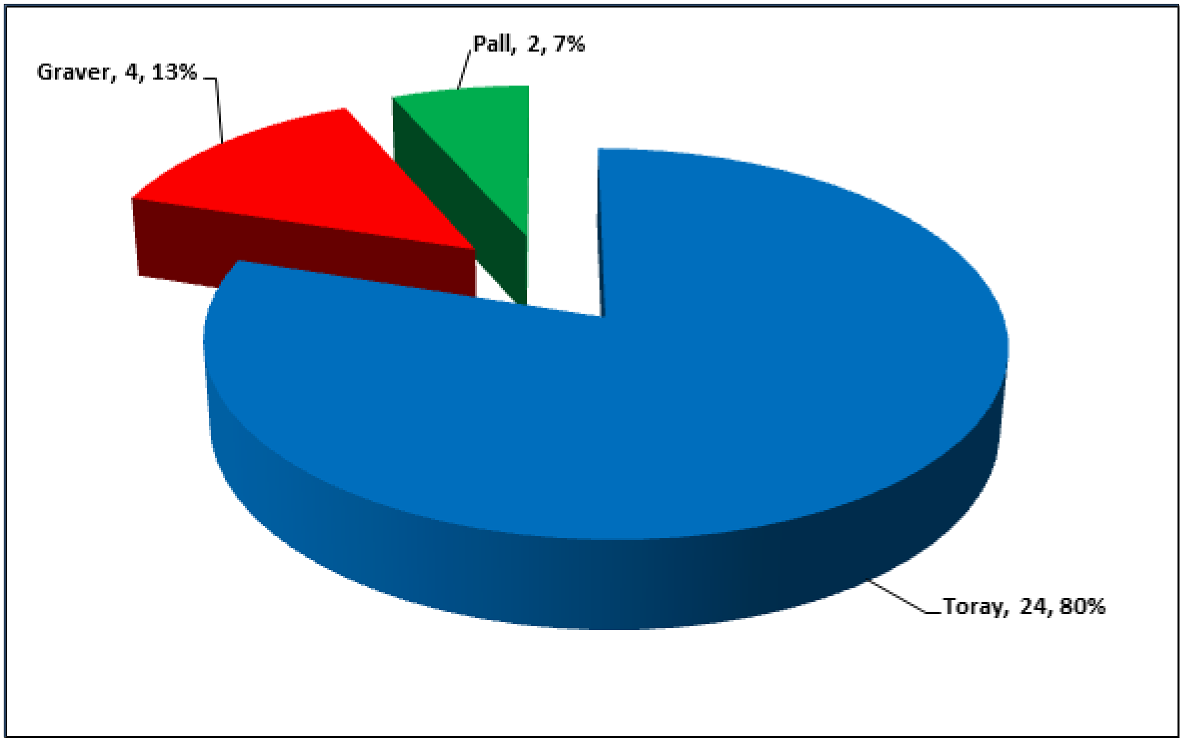

Figure 2-1
Percentage of Responses by Cation Ion Exchange Membrane Manufacturer Use

BWRVIP-190: BWR Water Chemistry Guidelines Impacts

The BWR Water Chemistry Guidelines Committee and the Mitigation Committee of the BWR Vessel and Internals Program (BWRVIP) issued the BWR Water Chemistry Guidelines [1] to provide proactive guidance for understanding key issues requiring monitoring of soluble impurities in feedwater, reactor water and other process streams. Within these guidelines, various limits and responses are prescribed for parameters requiring the use of ion exchange membranes for quantification of the concentration of species. Incorrect quantification could result in actions taken by chemistry or operation personnel that could impact corrosion control, fuel integrity, dose mitigation, or lead to incorrect assessments of system health.

Tables 6-5b, 6-5d and 6-5f of the BWR Water Chemistry Guidelines [1] provide guidance for reactor water under hydrogen water chemistry, noble metal chemistry and normal water chemistry regimes, respectively. No control parameters are directly identified that require the use of ion exchange membranes for quantification. However, reactor water conductivity can be corrected for soluble iron and zinc to determine if measured conductivity exceeding action levels is due to corrosive species, such as chloride and sulfate, or soluble iron or zinc which are innocuous to or reduce stress corrosion cracking.

Reactor water soluble Co-60, zinc, iron, copper and ion conductivity balances are provided as diagnostic parameters that would require use of cation exchange membranes.

Quantification of reactor water soluble Co-60 and soluble zinc is important for control of out of core dose rates in a BWR. Reactor water soluble Co-60 to soluble zinc ratios less than 2E-5 μCi/ml/ppb has resulted in stable or reduced dose rates. To achieve desired ratios, depleted zinc is added to the feedwater stream and the addition rate can be controlled by chemistry or operations personnel. Changes in the feedwater zinc addition rate are determined by analysis of reactor water soluble zinc, reactor water soluble Co-60, assessment of analysis results against industry and plant guidance, and limiting feedwater zinc concentrations to address fuel concerns.

Determination of other soluble and insoluble radioisotopes provides useful information for troubleshooting and evaluation of shutdown radiation field reduction programs. Trending of iron and copper establishes a basis for mass balances of metals in the steam cycle. Performing mass balances allows chemistry and engineering personnel to adequately assess and potentially identify areas of corrosion concern.

A good practice limit of less than 1 ppb is provided for reactor water soluble copper due to its interactions to reduce the effectiveness of hydrogen injection for mitigation of intergranular stress corrosion cracking. Impacts have been noted at reactor water soluble copper greater than 3 ppb.

Periodic ion-conductivity balances are recommended to estimate the concentration of unidentified and potentially corrosive ions. In order to perform a meaningful conductivity balance, soluble metals must be accurately quantified.

Table 6-6b of the BWR Water Chemistry Guidelines [1] provides control parameters for feedwater total iron, zinc and copper. As described above, accurate quantification of feedwater metals requires the use of an integrated feedwater or corrosion product sampler with a series of 0.45 μm membrane, cation exchange membrane and anion exchange membrane (if desired). Good practice and action levels are provided for these parameters as prior industry experience within these limits provides more reasonable assurance of fuel integrity. Operation outside these levels should occur only with concurrence of the fuels organization and fuel vendor. Inaccurate quantification could result in unnecessary or lack of corrective actions taken by the station to address fuel integrity or corrosion concerns.

PWR Primary and Secondary Water Chemistry Guideline Impacts

Guidance for PWRs, contained in the PWR Primary and Secondary Water Chemistry Guidelines, was developed by a committee of industry experts based on latest field and laboratory data to reduce equipment corrosion [2, 3]. Within these guidelines, boundaries for plant-specific optimization procedures are provided, some requiring use of ion exchange membranes to quantify concentrations of species. As with the BWR Chemistry Guidelines [1], incorrect quantification could result in actions taken, or lack thereof, by chemistry or operation personnel that could impact key system health, such as steam generator tube corrosion and thermal performance, and possibly outage radiation fields and outage duration due to an uncontrolled release of corrosion products.

Table 5-4 of the PWR Secondary Water Chemistry Guidelines [3] lists total iron and copper as control parameters for recirculating steam generator feedwater samples. The samples are collected using integrated sampling techniques described above. Feedwater corrosion product impurities, such as iron and copper, can affect various corrosion mechanisms in the steam generator tubes, such as pitting, intergranular attack, and stress corrosion cracking. Ensuring feedwater iron and copper are less than 5 ppb and 1 ppb, respectively, is crucial for ensuring that these corrosion mechanisms are minimized [3]. Information obtained from integrated corrosion product loading provides estimates for deposit loading and mass balances. Integrated corrosion product transport and lead assessments are listed as diagnostic parameters. The information is also used for evaluating the need for mechanical or chemical cleaning of steam generators.

Similar guidance is contained within Table 5-5 of the PWR Secondary Water Chemistry Guidelines [3] for once-through steam generator feedwater, with the exception of copper which is listed as a diagnostic parameter. Copper analysis is used for copper and copper oxide transport assessment. Even though most once-through steam generators have an all ferrous secondary cycle, baseline level of copper and copper oxide should be established [3].

Table 3-8 of the PWR Primary Water Chemistry Guidelines provides recommended chemistry surveillance during shutdown (reactor critical to flood up) of the reactor coolant system or CVCS letdown. The analyses given in the table are designed to characterize the behavior of various species in the cooldown, including filterable and non-filterable radioactive corrosion products and elemental iron and nickel [2]. Monitoring of such species allows for proper shutdown management for a controlled release of activated corrosion products. With uncontrolled releases, delays in refueling activities could be expected due to radiation fields above the refueling water surface. At some plants, total and filtrate fractions are determined in lieu of filterable and non-filterable species.

Additionally, Appendix F of the PWR Primary Water Chemistry Guidelines provides sampling and analysis considerations for corrosion products. The discussion includes methods for the use of cation membranes and 0.45 μm filter papers.

Quality Management

Generating technically valid results is a priority of all nuclear power plant chemistry laboratories. Producing quality data is achieved through a combination of procedures defining requirements to perform sampling, testing and maintenance, competent lab personnel, and validation of analytical methods, among others. The analytical methods employed at a nuclear power plant are selected to produce accurate and precise data to meet regulatory requirements, quantify concentrations relative to water chemistry guidelines [1, 2, 3] good practice and action level values, other system specifications defined in industry technical documents or plant chemistry optimization plans, and limitations of analytical equipment. Guidance for Quality Management Systems is provided in the Standard for a Power Plant Analytical Chemistry Quality Management System [6].

Method Validation

All methods employed by nuclear power plant chemistry laboratories should have undergone a battery of tests to determine the number of standards required for method calibration, verification of the calibration curve, verifying the limit of detections and blank interferences [6]. A change in cation ion exchange membrane manufacturer or type constitutes a change in a method's reagent or consumables that would require method re-validation. Completing a thorough method validation with new ion exchange membranes will help minimize risk towards impacts to the guidance contained in the Water Chemistry Guidelines [1, 2, 3] and maintaining data quality.

An acceptable method for validating a new method is to compare the results of new and existing methods on a common sample or standard. If the two methods are not statistically different from each other, then the new method may be deemed analytically equivalent. This validation method should be completed using the same matrix, which may require multiple comparisons for the various system process streams (i.e. feedwater, reactor water, stator cooling water, etc). A statistical method such as the Student's "t" test can be used [6]. Since plants have most likely been employing the same method for soluble radioisotopes and metals analyses, this comparison method may be best suited for this application. An example of a Student's "t" test is shown in Appendix A.

Before performing side by side comparison of the current methods with proposed methods, blank interference should be identified. As shown in Table 2-2 and discussed later in Chapter 4, the amount of metallic impurities between membrane filter manufacturers can vary significantly. Blank interferences should be identified, documented and resolved, or adjustments made, as appropriate [6].

Recovery studies can also be used to validate the new method [6]. Known concentrations of soluble metal species can be filtered and analyzed by AA, ICP, or XRF to determine the percent recovery. Recovery tests can also be completed using radioactive water. Limerick completed a recovery test in the early 1990s by using aliquots of reactor water diluted to one liter. During this study, Limerick also determined the efficiency of an elution procedure due to difficulties in filter digestion. In the elution process, the charged species were removed from the ion exchange membranes with a combination of 2N hydrochloric acid and 2N nitric acid.

The one liter sample was analyzed via gamma spectroscopy for total activity. Afterwards, the one liter sample was filtered through a series of filter paper and ion exchange membranes. The filters, filtrate and eluted filters were counted for activity to determine the capture and elution efficiency. The eluted filters were counted to determine how much activity was removed during the elution process. As with method comparison, multiple tests should be performed to determine statistical comparisons.

All method validations should be appropriately documented in accordance with the stations QA/QC program or change management procedures.

Preliminary results of various method validation and interface testing are discussed in further detail in Chapter 4.

Interlaboratory and Intralaboratory Programs

As part of quality management of chemistry data, all nuclear power plant chemistry laboratories should participate in interlaboratory and intralaboratory programs. The programs measure the proficiency of the laboratory and individual technicians. With interlaboratory programs, one laboratory's analytical capability is measured against other laboratories by comparing blind sample results for various parameters of interest at a nuclear facility.

Most nuclear power plant chemistry programs participate in NWT's Q-Chem Program for interlaboratory program compliance. The program provides samples similar to those expected at the respective plant type (i.e. BWR or PWR). With quantification of metals essential to a nuclear chemistry program, various filter standards are provided for analysis. Discussions with the vendor indicate that the program can be customized based on the direction and use of ion exchange membranes by the industry. Customizable programs can be created, including X-ray fluorescence calibration standards.

3
ION EXCHANGE MEMBRANE MANUFACTURERS

Technical data for available ion exchange membranes is discussed below. Specifications, test results, and comparisons shown in this chapter were provided directly by the vendor or available on their company website. Plant experiences with these filters will be discussed in detail in Chapter 4.

Toray Industries, Inc.

The Toray Industries, Inc. CP-1 and AP-1 ion exchange membranes are composed of cellulose fibers with long fibrous resins [4]. Polystyrene fibers were imbedded in a polyethylene matrix with the polystyrene functionalized with either anion or cation sites. When used with charged materials such as ion exchange resins, the charged fibers improved the removal of soluble materials [5].

The vendor-quoted value for static capacity is 0.83 meq per membrane. This was a significant improvement over the first generation of ion exchange membranes with impregnated powdered resin on the surface on standard filter paper. At this capacity, under normal conditions, saturation of the ion exchange filters should not be an issue for typical sampling volumes used in the feedwater, condensate, CVCS and reactor water, given their respective concentrations. The filters were provided as 47 mm diameter discs, fitting laboratory and in-line filter housings. Additional laboratory results for early Toray ion exchange membranes are shown in Tables 2-1 and 2-2 as well as in the Graver section below.

As shown in Figure 2-1, 80% of plant and utilities that responded to a recent industry survey use Toray ion exchange membranes. Mixed reviews towards filter digestion of Toray ion exchange membranes were reported. Some plants altered acid digestion practices while others developed elution techniques to satisfy data quality requirements.

In September 2012, information began circulating that Toray would discontinue manufacture of the CP-1 and AP-1 ion exchange membranes at the end of 2012, accelerating evaluation by plants and industry personnel for alternative ion exchange membranes. Some plants were already in the process of evaluating or using alternatives. Most recent information indicated that Toray would continue to supply ion exchange filters available for a number of years, lessening the urgency towards some plant transition plans.

Graver

Graver Nanodex™ ion exchange filter papers utilize a combination of fibrillated nanofibers and finely subdivided ion exchange resin media. The Nanodex™ ion exchange filter papers include an anion filter paper (AX 100) containing strongly basic, quaternary ammonium functional sites in the chloride form. The cation filter papers (CX 200) contain strongly acidic, sulfonic acid functional sites in the hydrogen form [5]. Scanning electron microscope (SEM) photomicrographs of the Graver Nanodex ™ ion exchange membrane surface and cross section are shown in Figures 3-1 and 3-2, respectively.

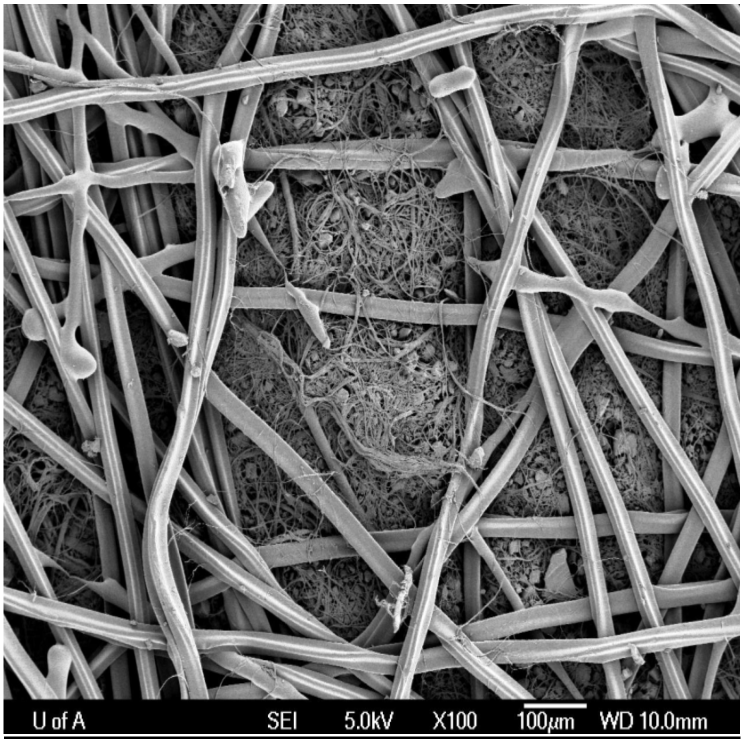

Figure 3-1
Graver Nanodex™ Cation Ion Exchange Membrane Surface SEM Photomicrograph [5]

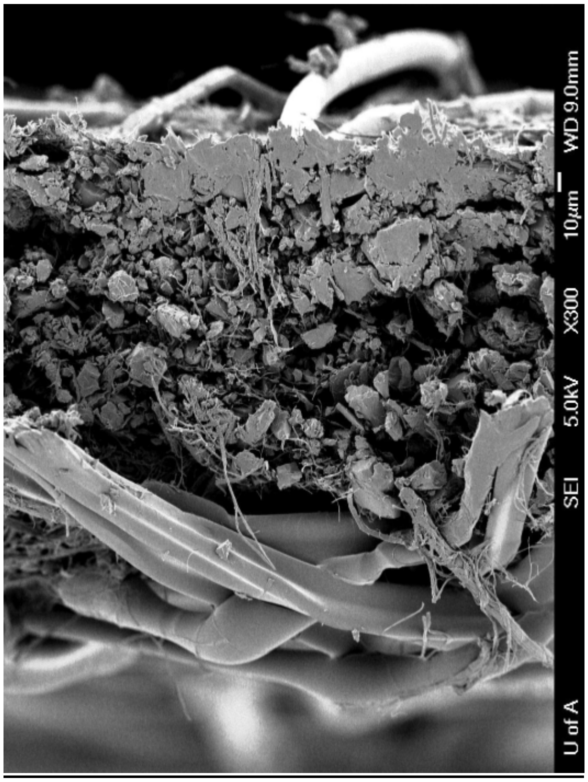

Figure 3-2
Graver Nanodex™ Cation Ion Exchange Membrane Cross Section SEM Photomicrograph [5]

The Nanodex™ ion exchange membranes are specifically designed for the nuclear power plant applications, with the new filter papers fitting standard bench top or in-line filter holders and housings [5]. The cation ion exchange membranes have reported ion exchange capacities slightly higher than the Toray cation ion exchange membrane. Additional specifications are shown in Table 3-1, and residual metal contaminants of interest are shown in Table 3-2. The manufacturing specification for the five transition metals listed in Table 3-2 is less than 6.0 ppm (µg/g) residual [5].

Table 3-1
Graver Nanodex™ Ion Exchange Membrane Specifications [5]

Property	Cation	Anion
Functional group	Sulfonic acid (H^+ form)	Quaternary ammonium (Cl^- form)
Capturable ions	Cations	Anions
Total ion exchange capacity, meq	0.90	0.60
Filter weight, mg	250	190
Filter thickness, µm	325	280
Diameter, mm	47	47
Unit weight, g/m^2	145	110
Chemical resistance	pH = 0 – 14	pH = 0 - 14

Table 3-2
Graver Nanodex™ Ion Exchange Membrane Residual Metal Contaminants [5]

Residual Metal	Cation (µg/g)	Anion (µg/g)
Iron	4.6	3.5
Nickel	0.4	None Detected
Chromium	2.6	1.7
Copper	2.5	1.9
Cobalt	2.5	1.3

Graver reported results from a battery of tests for qualification purposes of the Nanodex™ filters. Side by side comparisons between the Nanodex™, Toray CP-1, and in some cases Pall cation ion exchange membranes were completed for metal capture and elemental composition. For the metal capture study, a feed supply containing 0.47 ppm chromium, 1.15 ppm copper, 1.05 ppm iron and 3.35 ppm zinc as chloride salts was drawn through the filter paper under a light vacuum. Afterwards, the filters were dried, digested, and analyzed using an inductively coupled plasma (ICP) spectrometer. Sufficient feed was used to saturate the filter papers [5]. Results from the test completed by Graver are shown in Table 3-3.

Table 3-3
Graver Metal Capture Study [5]

Manufacturer	Trial	Chromium, g/kg	Copper, g/kg	Iron, g/kg	Zinc, g/kg
Graver	#1	0.310	4.08	54.0	0.018
Graver	#2	0.082	6.44	54.6	0.024
Toray	#1	0.054	4.36	36.5	0.017
Toray	#2	0.042	3.16	25.9	0.011
Pall	#1	0.143	2.53	13.8	0.013

Results of field trials at BWR and PWR stations were also reported [5]. Testing at the U.S. BWR occurred over the course of eight weeks, where Nanodex™ ion exchange membranes were compared along side Toray ion exchange membranes. Dissolved and particulate metals were analyzed using an ICP spectrometer. Field trials at a U.S. PWR were performed over eleven weeks, where samples were tested sequentially with installed filter papers on a weekly interval. The filter papers were installed using a 0.1 µm membrane, followed by the anion exchange membrane and then the cation exchange membrane. The entire filter array was analyzed as one sample [5]. Results from the BWR and PWR field trials are presented in Tables 3-4 and 3-5.

Table 3-4
Graver BWR Field Trial Results [5]

Date	Sample(1)	Form	Copper (ppb)	Nickel (ppb)	Zinc (ppb)	Chromium (ppb)	Cobalt (ppb)	Iron (ppb)
2/11/11	TC	Dissolved			12.432			
2/11/11	GC	Dissolved	0.45		8.054	0.243	0.468	1.964
2/18/11	TC	Particulate		1.140				2.560
2/18/11	TC	Dissolved		1.960	11.800		0.620	3.310
2/18/11	GC	Dissolved		0.900	11.800		0.560	1.300
2/25/11	TC	Particulate						4.425
2/25/11	GC	Particulate						3.571
2/25/11	TC	Dissolved		1.053	11.505	0.398		3.558
2/25/11	GC	Dissolved			11.929	0.257		1.171
3/4/11	TC	Particulate						1.930
3/4/11	TC	Dissolved			11.500	0.260		
3/4/11	GC	Dissolved	0.275		11.500			1.425
3/11/11	TC	Dissolved			11.500			1.270
3/11/11	GC	Dissolved			11.800			

Table 3-4 (continued)
Graver BWR Field Trial Results [5]

Date	Sample(1)	Form	Copper (ppb)	Nickel (ppb)	Zinc (ppb)	Chromium (ppb)	Cobalt (ppb)	Iron (ppb)
3/18/11	TC	Dissolved			11.545	0.209		
3/18/11	GC	Dissolved			12.091	0.182		
3/25/11	TC	Particulate						1.510
3/25/11	GC	Particulate						1.888
3/25/11	TC	Dissolved	0.210	0.970	14.300			3.450
3/25/11	GC	Dissolved	0.275		13.500			
4/1/11	TC	Dissolved			12.556			
4/1/11	GC	Dissolved			12.111			

(1)TC = Toray Cation; GC = Graver Cation

Table 3-5
Graver PWR Field Trial Results [5]

Date	Sample[(1)]	Iron (ppb)	Copper (ppb)	Lead (ppb)	Aluminum (ppb)	Calcium (ppb)	Magnesium (ppb)
Grab Samples							
5/5/11	Blank	10	5	30	5	10	5
5/5/11	TC	21	5	30	5	26	5
5/5/11	GC	33	5	30	5	115	53
5/5/11	GA	23	5	30	5	134	44
5/26/11	TA	13	<5	<30	13	<10	<5
Final Feedwater Samples							
5/19/11	TC	2.107	0.006	<0.003	0.003	0.014	0.019
5/19/11	GC	1.154	0.01	<0.004	0.001	0.043	0.014
5/26/11	TC	1.196					
5/26/11	GC	4.66					
6/2/11	TC	1.28	0.004				
6/2/11	GC	1.476	0.004				
6/9/11	TC	1.09					
6/9/11	GC	1.31					
6/16/11	TC	1.1					
6/16/11	GC	1.56					
6/23/11	TC	0.962					
6/23/11	GC	1.17					
6/30/11	TC	0.883					
6/30/11	GC	1.21	0.004	<0.00052	<0.00088	0.058	0.016
(1)TC = Toray Cation; GC = Graver Cation; TA = Toray Anion; GA = Graver Anion							

Graver reported that the BWR field trial results were statistically equivalent for parameters that were above the detection limits of the ICP spectrometer for, dissolved zinc, dissolved iron and particulate iron. For the PWR field trials results, Graver reported that the Nanodex™ cation ion exchange membranes averaged 45% higher particulate iron, 1.79 ppb, than the Toray cation ion exchange membranes, 1.23 ppb [5]. Increased particulate iron detected on the upstream 0.45 µm membrane may indicate different flow characteristics between the two ion exchange membranes. A statistical comparison of the BWR results is shown in Table 3-6.

Table 3-6
Graver BWR Statistical Field Results for Cation Exchange Membranes [5]

Parameter	Graver (ppb)	Toray (ppb)
Dissolved Zinc	11.6 ± 1.55	12.1 ± 1.03
Dissolved Iron	1.23 ± 0.37	1.90 ± 1.29
Particulate Iron	0.98 ± 1.28	1.84 ± 1.21

Pall

Pall Life Sciences provides various filters that are optimized for various sampling applications. In use currently by two utilities, the cation ion exchange membrane, I.C.E 450®, is a strongly acidic, negatively charged polysulfone membrane. Ion capacity is provided by a patented post-treatment process. The cation exchange membrane is supplied with hydrogen form sulfunoic acid active sites. The I.C.E 450® filters were made with and without a non-woven support. The SB-6407 anion exchange membrane is a strong base, positively charged membrane with quaternary ammonium groups. The SB-6407 is supplied in the chloride form. These filters, offered in a 47 mm diameter, have a 0.45 µm pore size and a thickness of 140 µm (5.5 mils). Both filters had properties suitable for the nuclear power plant application.

Information has recently been made available that Pall will no longer continue offering the I.C.E 450® and SB-6407 ion exchange membranes. However, Pall has other products that may serve as suitable replacements for both their ion exchange membrane filters.

Pall Mustang® ion exchange membranes utilize the principles of sorbent-based ion exchange chromatography on flat stock membrane. This provides ease-of-use and handling benefits over resin-based slurries in a manufacturing environment. The membranes are more specifically designed for biomolecule capture, plasmid preparation and endotoxin removal applications, but could provide high capacity for capture of charged metals and radioisotopes in a sample stream.

The ion exchange membranes are available in three chemistries: Q, S and E. The two products of interest for the nuclear application are the Q and S chemistry membranes. The strong anion exchange membrane (Q chemistry) is suited for removal of negatively-charge ions or proteins. The strong cation exchange membrane (S chemistry) purifies and concentrates positively-charged proteins and ions [7].

The Q chemistry membranes are 4.7 to 6.3 mils (119.4 to 160.0 µm) in thickness while the S chemistry membranes are 4.5 to 6.3 mils (114.3 to 160.0 µm) thick. The membranes are available in 8" x 10" sheets, requiring 47 mm diameter cuts to be made by chemistry personnel to fit in the standard filter holder apparatus. Custom roll, sheet and disc sizes are available.

Machery-Nagel

Machery-Nagel specializes in a variety of products for chemical analyses including filtration, rapid tests, water analysis, chromatography and bioanalysis. MN 616 LSA-50 and MN 616 LSB-50 ion exchange papers are included as part of their special filter papers product line.

Although no plants responding to a recent industry survey reported use of the Machery-Nagel product line, their ion exchange papers may be suitable in the nuclear power plant chemistry application. The MN 616 LSA-50 is an ion exchange filter paper with strongly acidic cation exchange resin. The filter paper is a matrix of polystyrene crosslinked with 8.5% divinylbenzene. The membrane is supplied in the hydrogen ion form of the sulfunoic acid active sites with a capacity of 2.0 meq/g.

The MN LSB-50 ion exchange filter paper uses strongly basic anion exchange resin. The filter paper is a matrix of polystyrene crosslinked with 6.0% divinylbenzene. The membrane is supplied in the hydroxide form with quaternary ammonium compounds. These filters have a capacity of 1.3 meq/g.

Sartorius

Sartorius, based in Germany, is a provider of laboratory and process technologies and equipment. Sartorius offers Sartobind® ion exchange membranes in 8.3" x 11.7" sheets. Q (quaternary ammonium functional sites) and S (sulfonic acid functional sites) technologies are available. The Sartobind® ion exchange membranes are made of stabilized reinforced cellulose materials. Binding sites are homogeneously grafted as a film on the inner walls of the cross-linked cellulose material. The current limiting factor with these ion exchange membranes is the pore size. The ion exchange membranes are considered macroporous, with a pore size specification of 3 to 5 µm. Additional information is required to determine if smaller pore sizes are available to better suit the needs of nuclear power plant applications. Vattenfall plants have recently tested Sartorius ion exchange membranes as part of their replacement evaluation. Additional data is presented in Chapter 4.

4

PLANT EXPERIENCES

In 2012, information became available that two primary vendors of ion exchange membranes may no longer manufacture products that are currently used in the nuclear power plant applications. As shown earlier in Chapter 2, nearly 80% of responses to a recent industry survey indicated that Toray was utilized as a cation ion exchange membrane supplier. With most plants understanding that their vendors may not provide their current filters, many began looking at different options based on preliminary testing from other utilities and vendors. Based on a recent survey concerning possible obsolescence of the major cation ion exchange membrane vendors, most plants were looking at Graver Nanodex™ filters as a possible replacement, as shown in Figure 4-1. Plant experiences with various ion exchange membrane vendor products are summarized below.

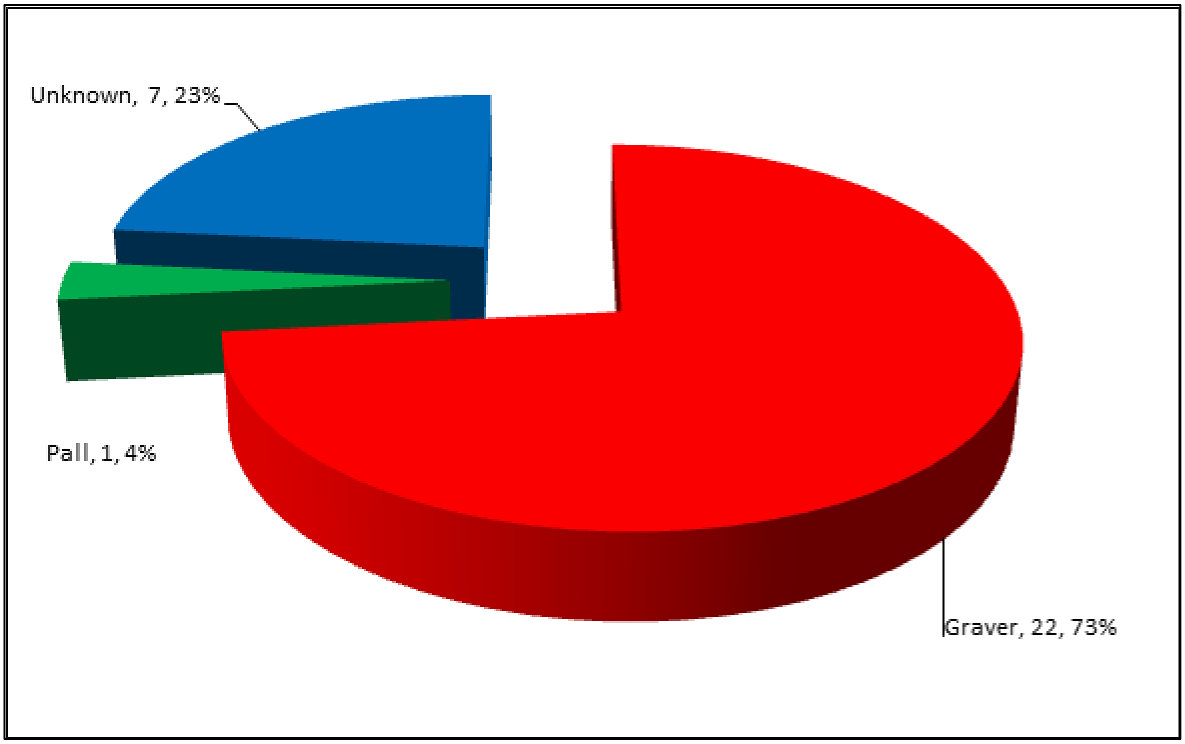

Figure 4-1
Percentage of Response for Future Manufacturer Use

Limerick

When Gelman discontinued their ion exchange membrane line in the early 1990s, Limerick performed a series of tests with the Toray cation ion exchange membranes. Due to difficulty with digesting the Toray filters with acid and heat, the plant decided to try eluting the metals and radioisotopes from the ion exchange membranes. The capture efficiency and elution efficiency were quantified prior to implementing the Toray cation ion exchange membranes.

Efficiency was determined by using aliquots of reactor water, diluted to one liter. The one liter sample was analyzed using gamma spectroscopy to determine the initial activity (total and individual isotopes). Afterwards, the sample was filtered through a filter stack of one Millipore 0.45 µm filter paper, one Toray cation filter and either one or two Gelman anion filters. The filter stack and filtrate were counted using gamma spectroscopy to determine the total activities removed. The Millipore and ion exchange membranes were separated and counted individually. The ion exchange membranes were then eluted with a combination of 2N hydrochloric acid and 2N nitric acid. Afterwards, the ion exchange membranes were recounted to determine how much activity was not recovered. The results of the ion exchange (IX) efficiency tests are shown in Tables 4-1 and 4-2. The results presented are for one sample. The plant reported that using a filter stack with two anion filters resulted in greater than 90% efficiency for ions of interest.

Table 4-1
Limerick Ion Exchange Recovery Results

Isotope	**Cr-51 (µCi/ml)**	**Co-58 (µCi/ml)**	**Co-60 (µCi/ml)**	**Zn-65 (µCi/ml)**	**I-131 (µCi/ml)**	**Ba-140 (µCi/ml)**	**Total Activity (µCi/ml)**
Filter Stack: 1 0.45 µm filter – 1 Toray cation filter – 1 Gelman anion filter							
Initial Activity	14.78	0.2402	0.1271	0.5072	0.02502	0.03365	20.131
Total Captured	10.012	0.1993	0.0994	0.4238	0.01201	0.02127	12.574
Activity Filtrate	4.4076	0.001106	0.003419	0.002481	0.01177	---	6.411
Eluted IX Filters	6.627	0.001861	0.000982	0.06172	0.008756	0.005726	6.997
Particulate Activity	0.0814	0.004141	0.002995	0.006315	---	---	---
Filter Stack: 1 0.45 µm filter – 1 Toray cation filter – 1 Gelman anion filter							
Initial Activity	13.913	0.2238	0.1168	0.4772	0.02104	0.02657	45.415
Total Captured	13.45	0.2145	0.1051	0.4307	0.02024	0.01401	16.671
Activity Filtrate	1.043	0.000659	0.001279	---	0.003456	---	2.236
Eluted IX Filters	9.751	0.003584	0.001964	0.1395	0.01563	0.006422	10.4
Particulate Activity	0.04874	0.00595	0.003335	0.01012	---	---	0.07663

Table 4-2
Limerick Ion Exchange Capture and Elution Efficiencies

Isotope	Cr-51 (%)	Co-58 (%)	Co-60 (%)	Zn-65 (%)	I-131 (%)	Ba-140 (%)	Total Activity (%)
Filter Stack: 1 0.45 µm filter – 1 Toray cation filter – 1 Gelman anion filter							
Capture Efficiency	67.7	83.0	78.2	83.6	48.0	63.2	62.5
Elution Efficiency	33.3	99.0	99.0	85.2	27.1	73.1	44.4
Total Efficiency	24.3	82.4	78.0	73.3	17.1	52.5	31.5
Filter Stack: 1 0.45 µm filter – 1 Toray cation filter – 1 Gelman anion filter							
Capture Efficiency	96.7	95.8	90.0	90.3	96.2	52.7	36.7
Elution Efficiency	27.2	98.3	98.1	66.8	22.8	54.0	37.3
Total Efficiency	23.1	94.3	88.5	---	10.5	39.9	30.0

Cooper

Cooper has used Toray cation exchange filter paper as part of their feedwater system sampling protocol for several years. For feedwater zinc analysis, Cooper utilizes an ICP spectrometer following acid digestion of the feedwater integrated filters. Since 2008, Cooper's annual median feedwater soluble zinc has ranged between 0.30 and 0.35 ppb utilizing this method.

In October 2012, Cooper ran out of available Toray cation ion exchange membranes at the plant and began using the Nanodex™ CX 200. As shown in Figure 4-2 below, reported feedwater zinc decreased from 0.2 ppb to 0.02 ppb when the transition to the Nanodex CX 200 cation ion exchange membranes occurred. There were no zinc injection process or plant operating changes that could account for the decrease. These plant results confirmed earlier laboratory testing that also showed low recovery for zinc when a known concentration of metals was filtered through the filter stack consisting of a 0.45 µm membrane and a cation ion exchange membrane.

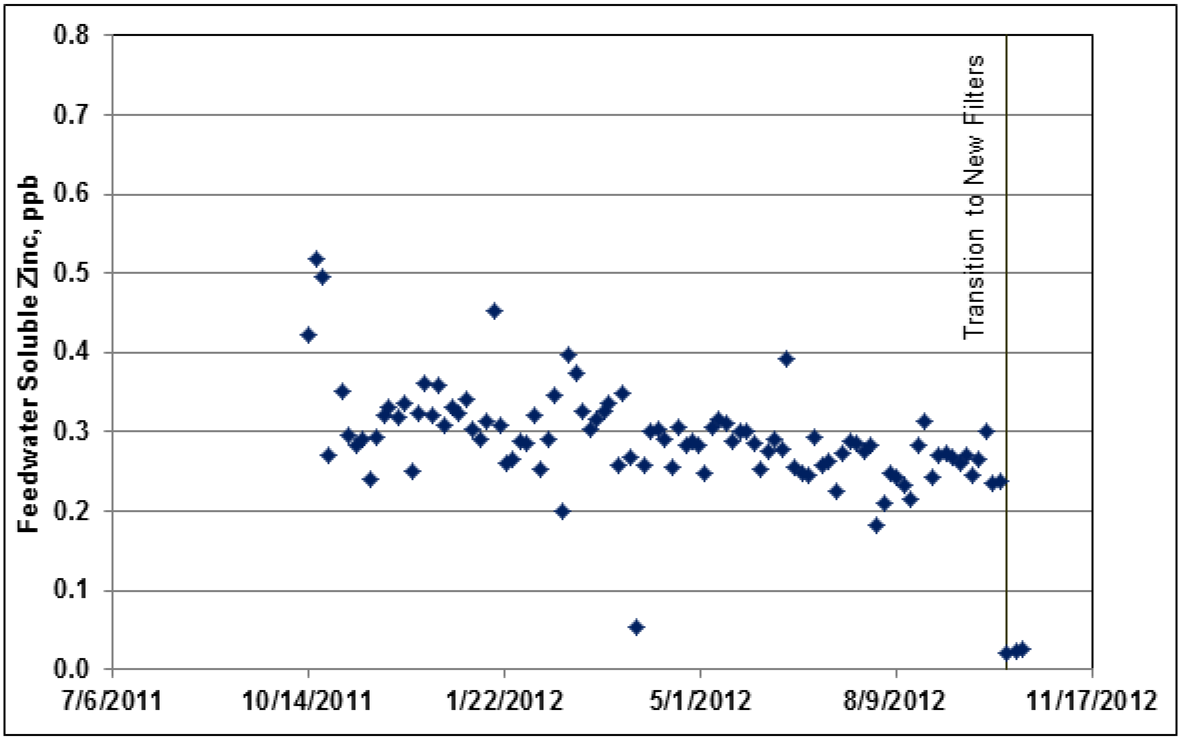

Figure 4-2
Cooper Feedwater Soluble Zinc before and after Filter Manufacturer Transition

Cooper is currently working with the vendor for resolution of the low recovery.

Monticello

Most, if not all, plants include a blank set of filters as part of their metals analyses to account for the normally minor trace metal contamination. Results from the blank filters are typically included in the metals concentrations calculation to remove trace contamination as a potential interference.

For metals analysis, Monticello uses X-ray fluorescence for analysis of filters after they have been dried. Monticello's experience has shown that the amount of iron, copper, nickel and zinc left behind on a blank set of Toray filters after rinsing with deionized water was well under 1 µg. However, the Nanodex CX 200 cation ion exchange filters showed higher than expected levels of nickel and zinc as shown in Table 4-1. For these tests, two filters were rinsed with 1500 mL of deionized water while two others were analyzed without rinsing.

Table 4-3
Monticello Trace Metal Contamination Test Results

Element	Bag #1 (Rinsed)	Bag #2 (Unrinsed)	Bag #3 (Rinsed)	Bag #4 (Unrinsed)
Chromium, µg	<LLD	0.191	1.393	1.257
Iron, µg	<LLD	<LLD	<LLD	<LLD
Cobalt, µg	<LLD	<LLD	<LLD	<LLD
Nickel, µg	6.209	7.004	6.058	6.636
Copper, µg	55.053	<LLD	<LLD	<LLD
Zinc, µg	21.393	13.235	13.754	13.951
LLD = Lower Limit of Detection				

To perform sampling for filterable and non-filterable species, Monticello uses a Millipore 0.45 µm filter paper on top of the cation ion exchange membrane. When comparing the filter stacks using Toray cation ion exchange membranes to the filter stack with Nanodex CX 200, visible distribution characteristics were observed on the 0.45 µm membrane filters as shown in Figure 4-2. This could indicate problems with uniform flow through some cation ion exchange membranes.

Figure 4-3
Color Comparison of Monticello Membrane Filters

Although it is not visible in Figure 4-2, the filter on the far left is the Nanodex cation exchange membrane. Technicians were challenged with separating the Nanodex filter from the Millipore 0.45 µm filter paper, with the Nanodex filter appearing to come apart. Results from Monticello have been provided to the vendor for resolution.

Dresden

Recovery tests were performed at Dresden 2 and 3 using reactor water to compare the Toray cation ion exchange membrane to the Nanodex CX 200. Results of the recovery tests are shown in Tables 4-2, 4-3 and 4-4. The data presented in Tables 4-2 and 4-3 are from samples collected during power operation. Two liters of reactor water will filtered through the filter stack before analysis via X-ray fluorescence. The Dresden 3 data presented in Table 4-4 is from a shutdown period, with one liter of reactor water used for side by side comparison.

Table 4-4
Dresden 2 Online Reactor Water Recovery Tests

Parameter	Toray	Graver
Iron, µg	0	16.9
Copper, µg	3.1	2.7
Zinc, µg	38.4	14.9

Table 4-5
Dresden 3 Online Reactor Water Recovery Tests

Parameter	Toray	Graver
Chromium, µg	4.4	4.2
Iron, µg	167.4	146.0
Cobalt, µg	1.3	0.5
Nickel, µg	5.2	0.5
Copper, µg	75.9	51.7
Zinc, µg	80.7	31.9

Table 4-6
Dresden 3 Shutdown Reactor Water Recovery Tests

Parameter	Toray	Graver
Copper, µg	39.9	5.7
Zinc, µg	34.4	8.6

For the Dresden recovery tests, the metals capture on the Graver Nanodex filters was consistently lower than for the three tests than the Toray cation ion exchange, with one exception. In the Dresden 2 online recovery test, the Graver product yielded 16.9 µg iron while none was detected on the Toray cation ion exchange membrane. The low recovery results for Dresden were similar to those experienced at Cooper.

Vattenfall

Ringhals and Forsmark use Pall I.C.E 450® cation and SB-6407 anion exchange membranes for soluble radioisotopes and metals. As discussed in Chapter 3, Pall has announced that they would discontinue these ion exchange membranes. Vattenfall plants have begun examination of various vendor products to replace the current Pall ion exchange membranes.

Vattenfall did a side by side comparison of their current Pall ion exchange membranes with the Graver Nanodex™ membranes. Results of the comparison are shown in Figure 4-3.

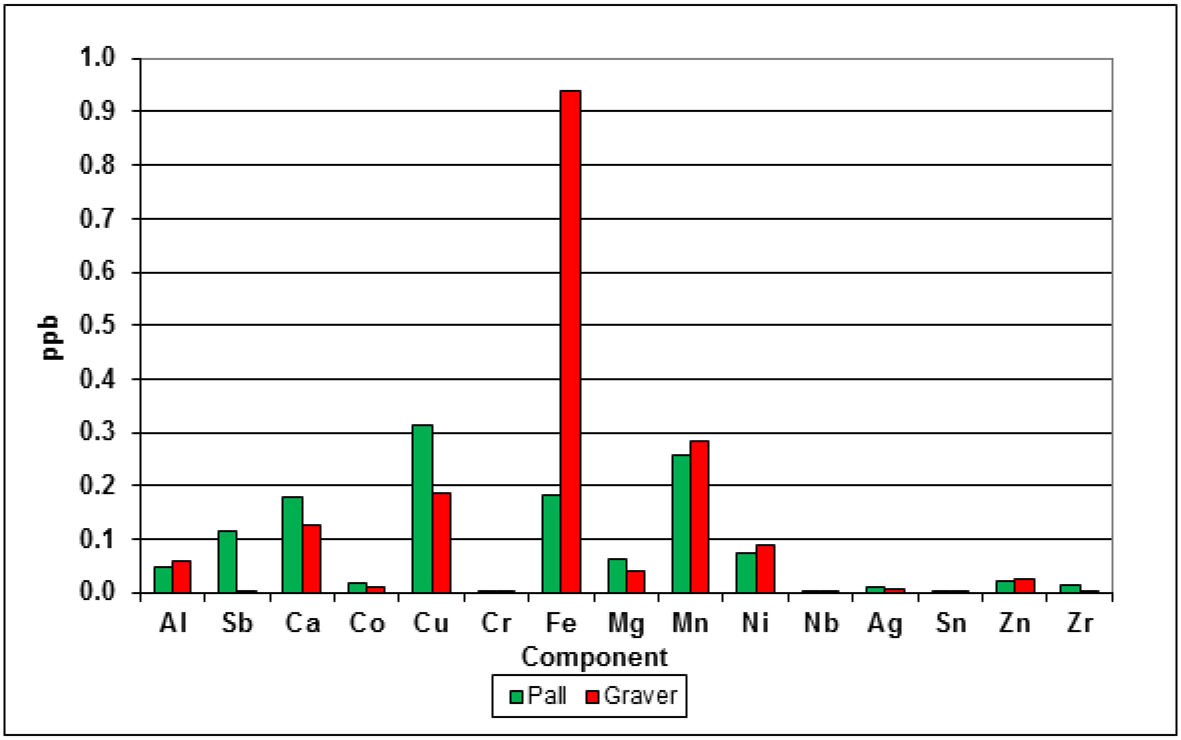

Figure 4-4
Vattenfall Reactor Water Metals Cation Exchange Membrane Comparison

In most cases, there were reasonable comparisons of metal components between the Pall and Graver products. However, there were noticeable differences with iron and antimony. Antimony is considered hard to measure by the utility and has high detection limits. It may not be reasonable to compare antimony results with other elements.

As shown in Figure 4-5 and similar to Figure 4-4, the Graver products show a high level of iron in the blank filters. Sartorius filters were also included in the trace metal contamination testing. Negative values shown indicate that the contaminant levels are below the detection limit for the methods used by the utility. Negative values should be discounted.

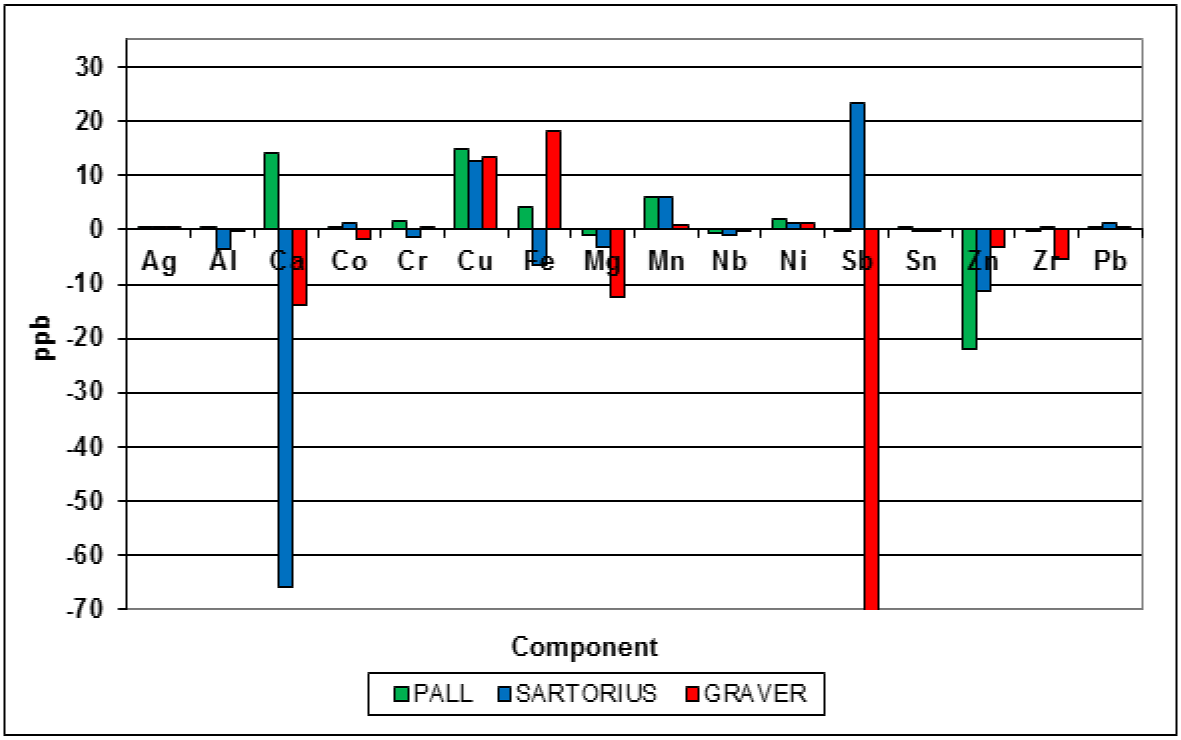

Figure 4-5
Vattenfall Reactor Trace Metal Contamination Test

Graver filters showed significant iron contamination compared to the Pall and Sartorius filters. The Pall filters showed high levels of calcium contamination. Similar to antimony, calcium is also considered as a hard to detect element with high detection limits. Calcium results should not be used for comparison. Each cation exchange membrane showed similar copper contamination.

Vattenfall also reported issues with filter digestion using their current digestion method. Using vendor recommendations for digestion with nitric acid, improvements were noted in the digestion procedure, but the digestion of the Pall filters did not show improvement.

Oconee

Oconee was one of the first nuclear plants to adopt full use of the Graver Nanodex™ filters. No recovery tests were performed at the station to support the transition. As shown in Figure 4-6, no changes were observed in baseline soluble feedwater copper or lead when the Graver Nanodex™ filters were placed into service in February 2012. Oconee has no major components with copper materials and lead has been historically low at the plant.

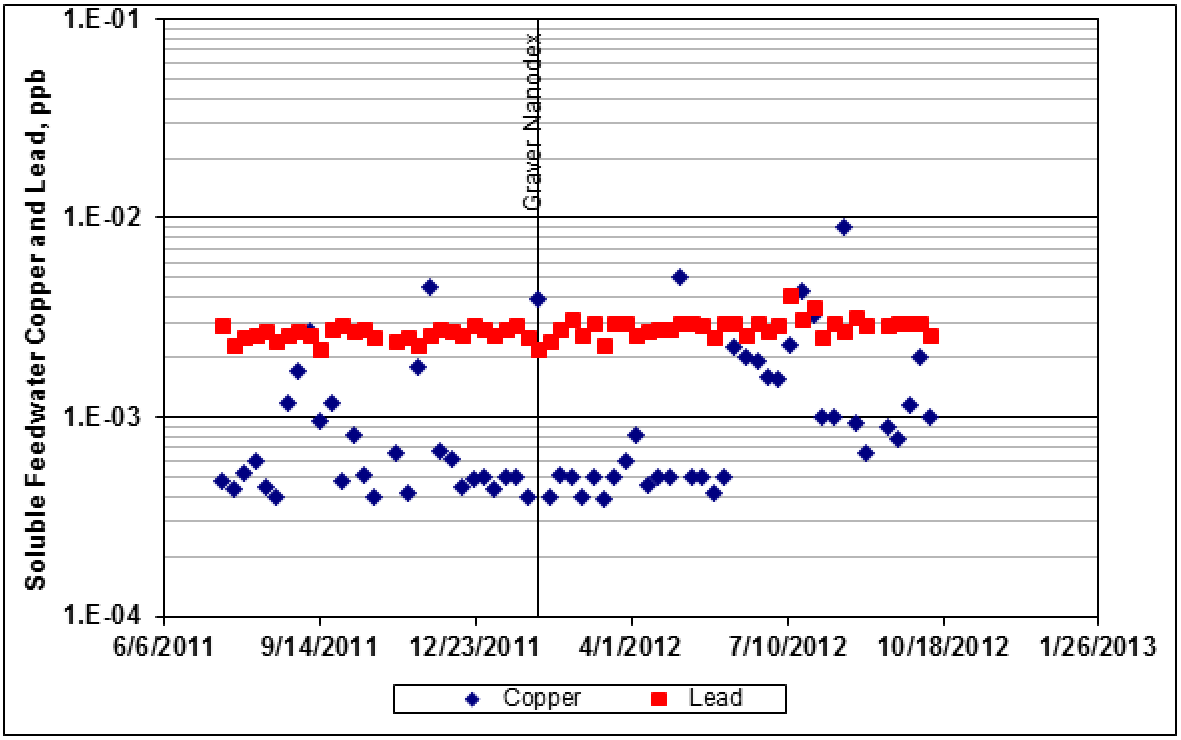

Figure 4-6
Oconee Baseline Soluble Feedwater Copper and Lead Before and After Graver Filter Use

Graver Nanodex™ filters remain in use at Oconee and some other Duke Energy facilities.

Callaway

Callaway completed sequential tests of Toray and Graver cation ion exchange membranes as part of their transition plan away from Toray. The results for iron, shown below in Table 4-5, were documented in their iron transport database. Comparable results were achieved between the Toray and Graver products.

Table 4-7
Callaway Iron Comparison between Toray and Graver

	Toray	Graver
#1	0.954	0.810
#2	0.711	0.720
#3	0.830	0.708
#4	0.830	1.04
#5	---	0.820
Average	0.831	0.820

Summary and Future Work

From the available plant experiences, one of the most common issues observed when comparing the performance of ion exchange membranes from various vendors was differing recoveries. As was seen at Cooper and Dresden, the difference in recovery amounts can be significant. In most cases, recovery was lower with Graver than for Toray. Resolution is still required to understand why both plants saw low recovery for various metals, which was not consistent with field trials reported by Graver. Additional data may be required to achieve resolution.

Additional plant data are required in order to perform statistical analyses of the performance of ion exchange membranes from different vendors. To determine if ion exchange membranes perform comparably in a given laboratory method, multiple ion exchange membranes should be analyzed in a similar matrix so that a statistically significant testing can be performed. An example of a statistical test is provided in Appendix A.

Monticello and Vattenfall also documented issues with high blank contamination on ion exchange membranes. Monticello had historically measured blank contamination of less than 1 µg for metals but have seen higher than expected amounts of nickel and zinc on cation exchange membranes, with and without rinsing. Monticello has provided information to the vendor for resolution.

Consideration should be given to development of a qualification program to be performed by an independent lab that would encompass tests on the characteristics of various ion exchange membranes. Test could include recovery efficiency, capacity determination, thickness, metallic impurities, resin dispersion, etc. Test conditions such as sample volumes, sample temperature and filtration flow rate would be specified and reported. Methodologies for acceptable digestion of ion exchange filters for use with AA or ICP analyses would be determined. The suitability of each ion exchange membrane for analysis by XRF would also be determined.

5
RECOMMENDATIONS AND CONDITIONS TO AVOID

Recommendations

The following recommendations are based on utility and vendor experience documented in this report. These recommendations will help minimize the risk of systematic data errors in chemistry results that are used to meet objectives and guidance established in the Water Chemistry Guidelines [1, 2, 3]. If adequate quality management is applied, little to no impact should occur to current industry guidance.

1. Compare analysis methods used with current ion exchange membranes to those with alternative ion exchange membranes. Comparison should be made using the same matrix, which may require multiple comparisons for various system process streams.

2. Collect sufficient data during side by side testing to perform a statistical comparison of the ion exchange membranes. A statistical test such as the Student's "t" test can be used. An example of a Student's "t" test is provided in Appendix A.

3. Prior to performing side by side testing, blank contaminants should be identified for the various ion exchange membranes to be tested as they may vary significantly. Blank interferences should be documented, resolved or adjustments made as appropriate.

4. Recovery or capture studies should be completed. Recovery tests can include filtering a sample with known concentration of metals through a filter stack containing ion exchange membranes and determining how much is recovered on the filters. Limerick took an approach of utilizing aliquots of reactor water diluted to one liter so that recovery can be determined via gamma spectroscopy.

5. Consideration should be given to development of a qualification program to be performed by an independent lab that would encompass tests on the characteristics of various ion exchange membranes. Test could include recovery efficiency, capacity determination, thickness, metallic impurities, resin dispersion, etc. Test conditions such as sample volumes, sample temperature and filtration flow rate would be specified and reported. Methodologies for acceptable digestion of ion exchange filters for use with AA or ICP analyses would be determined. The suitability of each ion exchange membrane for analysis by XRF would also be determined.

6. Document method validation results in accordance with the station or utility QA/QC procedure. Other tools could be utilized such as the Corrective Action Program, Engineering Change, or Change Management Program.

7. For plants that are not currently considering a change in ion exchange membrane product, it may be prudent to validate alternative ion exchange membrane filters for lab use in the event

that current membranes become obsolete or cannot be obtained in a timely manner to maintain inventory.

8. Transitions in ion exchange membrane use should be made proactively. Ensure adequate inventory of current and proposed ion exchange membranes to complete method re-validation tests, recovery and blank determinations as well as maintaining current monitoring requirements specified in plant procedures.

6

REFERENCES

1. *BWRVIP-190: BWR Vessel and Internals Project, BWR Water Chemistry Guidelines – 2008 Revision*. EPRI, Palo Alto, CA: 2008. 1016579.
2. *Pressurized Water Reactor Primary Water Chemistry Guidelines: Volume 2, Revision 6*. EPRI, Palo Alto, CA: 2007. 1014986.
3. *Pressurized Water Reactor Secondary Water Chemistry Guidelines – Revision 6*, EPRI, Palo Alto, CA: 2004. 1008224.
4. D.E. Farmer, LL Sundberg, and M.R. Alkowni, "Evaluation of New Cation Papers," presented at the BWR Chemistry Workshop IV, San Jose, CA (February 26 – March 1, 1990).
5. P. A. Yarnell, "Nanodex™ Filter Papers," paper presented at International Water Conference, San Antonio, Texas, November 4-8, 2012.
6. *Standard for a Power Plant Analytical Chemistry Quality Management System*. Power Plant Chemistry Advisory Group. 2009.
7. *Pall Ion Exchange Membranes*. Pall Life Sciences, Ann Arbor, MI: 2012. Product ID 47475.
8. Samuel B. Richmond. *Statistical Analysis*. Ronald Press, U.S. 1964, p. 576.

A

STATISTICAL TEST EXAMPLE

When a change in ion exchange membrane is considered, re-validation of analysis methods should be performed. By doing so, reasonable assurance can be obtained that data quality will not be compromised. An acceptable means of validating a method is to compare the proposed method (i.e. one with new ion exchange membrane) to that current method. Comparison should be made utilizing the same matrix, which may require multiple comparisons to ensure all process streams (reactor water, feedwater, CVCS, etc.) are covered.

Multiple analyses should be performed over a period of time and, if possible, by multiple qualified analysts. Individual analysis of the two methods should be performed side by side using the same prepared standard. Once the data population is obtained, the averages and standard deviations for each method should be calculated, as shown in Table A-1.

Table A-1
Example of Data Population with Averages and Standard Deviations

	Existing Membrane Method	New Membrane Method
Sample 1, ppb	0.81	0.92
Sample 2, ppb	0.95	0.90
Sample 3, ppb	1.06	0.84
Sample 4, ppb	0.85	0.87
Sample 5, ppb	0.87	1.04
Sample 6, ppb	0.91	0.65
Sample 7, ppb	0.70	1.25
Sample 8, ppb	0.85	1.14
Sample 9, ppb	0.96	1.13
Sample 10, ppb	1.10	1.04
Average, ppb	0.91	0.98
Standard Deviation, ppb	0.12	0.18

In order to confirm whether the two methods provide similar analytical results, a statistical “t” test should be performed. The “t” value should be calculated and compared to the critical “t” values contained in statistical analysis handbooks, corresponding to degrees of freedom in the test case. The “t” value can be calculated by first calculating an estimated standard deviation of the combined population set by:

$$S_{ab} = \sqrt{\frac{(n_a - 1)S_a^2 + (n_b - 1)S_b^2}{n_a + n_b - 2}}$$

Where:

S_{ab}	Combined standard deviation
n_a	Number of results for existing method
n_b	Number of results for new method
S_a	Standard deviation for existing method
S_b	Standard deviation for new method

In this case, with ten sample results for each method, the combined standard deviation was calculated to be 0.15. With the combined standard deviation, the "t" value is calculated by:

$$t_{calculated} = \frac{|\overline{X_a} - \overline{X_b}|}{S_{ab}\sqrt{\frac{1}{n_a} + \frac{1}{n_b}}}$$

Where:

$\overline{X_a}$	Average of results for existing method
$\overline{X_b}$	Average of results for new method

In this case, the calculated "t" value is 1.07. The critical "t" values can obtained from most statistical analysis handbooks, reference [8] for example. Using a two-tailed distribution, the critical "t" value found for 95% confidence with 18 degrees of freedom ($n_a + n_b - 2$) is 2.101 [8]. Since the calculated "t" value is less than the lookup value, it can be accepted with confidence and the two analytical methods can be considered comparable. If the calculated "t" value were greater than the critical "t" value, then the method should be rejected.

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