



The R&D Notebook

A publication of the Laboratory Water Division of Millipore

June 1998

Optimizing Storage of Purified Water for Laboratory Applications

Daniel Darbouret ⁽¹⁾, Ichiro Kano ⁽²⁾, Elodie Youf ⁽¹⁾ and Byron Stewart ⁽³⁾

(1) Research & Development, Laboratory Water Division, Millipore S.A., St Quentin en Yvelines, France

(2) Research & Development, Laboratory Water Division, Nihon Millipore Ltd., Tokyo, Japan

(3) Laboratory Water Division, Millipore Corporation, Bedford, MA, USA

Abstract: Due to low flow, volume demands and production limits in laboratory scale water systems, storage of pure water is often a necessary step in the production of ultrapure water. The different solutions used by industry to limit water degradation during storage are not always efficient and, overall, are not applicable to laboratory scale systems.

The present study looks at the various criteria needed to have a storage vessel suited to high purity water in a laboratory. It shows that pure water quality can be relatively well maintained during storage in terms of resistivity, TOC and bacterial contents when appropriate construction materials are selected and qualified accessories are used to prevent airborne contamination and internal biofilm formation.

Introduction

A wide variety of substances may be found in natural and potable water supplies. Technologies, such as reverse osmosis, ion-exchange and distillation, are used to purify water which is then used immediately or stored for later use or additional purification. Storage causes a decrease in water purity due to the re-contamination by ions, organics, microorganisms and particulates from the external environment and from the storage container itself¹.

HPLC trace enrichment techniques were used to monitor the amount of organics in water stored in various types of containers². Starting with high purity water, it was shown that organics can be detected as little as one hour after storage in plastic containers. Organics can also be detected even when water was stored in glass. Special storage bottle preparation must be developed to minimize contamination for many analytical studies³.

Similar contamination challenges occur in life science applications. For example, the effects of ultrapure water storage in glass on zygote development to the

blastocyst stage have been examined⁴. The frequency of development to the blastocyst stage for fresh ultrapure water was significantly higher than that of water stored for 7 to 14 days. Early development of bovine embryos was seriously altered by the purification method and the storage period of that water.

Water quality effects are also noticeable in interfacial surface chemistry studies⁵. Impurities seem to affect the surface potential of the expanded monolayer.

All of these ultrapure water applications demand an increased awareness of water storage conditions which affect final polishing performance.

Many applications involving ultrapure final polishing have volume or flow demands which necessitate a large storage reservoir. In the pharmaceutical and microelectronics industries, process engineers strive to reduce degradation using techniques, such as recirculation through UV lamps and sterilizing filters, nitrogen blankets and vent filters.

MILLIPORE

However, these techniques have varied effectiveness, are expensive and have limited compatibility with laboratory water systems designed to produce from 10 to 200 liters per day.

The purpose of this study is to define conditions which optimize pure water storage, and to integrate the techniques and hardware into a reservoir storage system suitable for the research, analytical or quality control laboratory.

Raw Materials Selection

Extractable studies

Various materials may be used to construct reservoirs. Materials which minimize organic and ionic extractables must be selected.

The common plastics available contain a number of additives including antioxidants, stabilizers, plasticizers, lubricants, coloring agents and impact modifiers^{6,7}.

During the development of storage reservoirs and water purification systems at Millipore, several plastics were analyzed via controlled extractable experiments. Extractable data was developed for polypropylene, three forms of high density polyethylene (HDPE1, HDPE2, HDPE3), Halar®, and for polyamide/glass fiber composite.

Procedure

Raw materials were supplied as pellets. Five grams of each polymer sample were placed in 100 ml of Milli-Q® ultrapure water at 18.2 MΩ.cm and less than 10 ppb TOC (total organic carbon) in PFA bottles. The bottles were soaked and rinsed in ultrapure water 10 times. The extraction was then performed with 50 ml of ultrapure water at 37 °C for 24 hours before the first measurement. The water was filtered through a 0.45 μm membrane filter to remove particles and analyzed. Ions were analyzed via ion exchange chromatography (Yokogawa IC-7000) and TOC levels were evaluated via a Shimadzu TOC 5000 Analyzer. The extraction study was repeated over three days to follow the initial release of extractables.

Results

When performing extractable tests on raw pellets, the extraction surface area and incubation temperature were higher than that in the actual product application; these experimental conditions accelerate leaching, and allow extractable concentrations to be predicted or measured over time. Such extractable profiles for specific materials provide good indicators

for rinse up and continuous extractable levels in the finished product.

Water has been analyzed after various storage conditions. The effect of materials in contact with water, retention of airborne contaminants and UV radiation on microbiological growth were examined. The corresponding results and a summary of the final qualification process are discussed.

Table 1 displays ionic species in filtered water for two polymers : polyamide/glass fiber and Halar®.

The limit of detection for anions is 0.1 ppb (except PO₄²⁻ at 1 ppb). The limit of detection for cations is 1 ppb (except Mg²⁺ at 0.1 ppb). <0.1 or <1 indicates that the measured ion concentration is below the respective limit of detection. The total absence of an ion (no detectable peak) is indicated as "nd".

Halar®, a fluorinated compound (confirmed by the relatively high fluoride concentration seen after three days of extraction) is a very clean material which can be used to manufacture small components.

Table 2 contains data from plastic materials commonly used for the manufacture of storage tanks. There was no significant difference in ionic release among the various raw material pellets.

Material	Polyamide/Glass fiber			Halar®		
	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
Fluoride	36.4	20.5	14.8	73.3	30.8	26.5
Chloride	274.3	46.2	22.2	4.1	0.6	0.5
Nitrite	15.7	2.3	0.3	0.4	0.4	nd
Phosphate	nd	nd	nd	nd	nd	nd
Bromide	1.8	1.8	1.8	nd	nd	nd
Nitrate	645.4	258	138	4.8	0.3	nd
Sulfate	432.4	168	94.8	2.9	0.5	nd
Calcium	645.9	309	198	119	< 1	< 1
Magnesium	51.9	26.4	20.6	2.8	< 1	< 1
Potassium	2630	3795	2018	0.8	< 1	< 1
Sodium	71	173	101	3.9	1	< 1
Aluminum	24.2	3.2	3	<1	nd	nd
Chromium	nd	nd	nd	nd	nd	nd
Iron	nd	nd	nd	nd	nd	nd
Copper	81.9	113	95.4	nd	nd	nd
Zinc	0.8	nd	nd	0.5	nd	nd
Lead	nd	nd	nd	nd	nd	nd
Nickel	nd	nd	nd	nd	nd	nd

Table 1 : Ionic extractables from Halar® and polyamide/glass fiber composite (in ppb)

Material	1			2			3			4		
	HDPE1			HDPE2			HDPE3			Polypropylene		
Ion	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
Fluoride	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Chloride	11.7	0.9	0.5	0.7	1.4	0.4	1.6	0.7	0.3	6.0	3.8	2.2
Nitrite	2.2	0.5	< 0.1	nd	nd	nd	0.4	nd	nd	0.3	nd	nd
Phosphate	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Bromide	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Nitrate	1.4	0.3	< 0.1	nd	0.4	< 0.1	0.5	0.3	< 0.1	1.3	1	0.7
Sulfate	6.2	0.4	0.1	0.7	0.3	< 0.1	1.7	0.4	0.2	1.1	1.1	1
Calcium	9	2	1	7.8	2.1	1	12	3.3	1	5.0	1	1
Magnesium	1.7	0.3	< 0.1	0.2	0.1	< 0.1	0.3	0.1	< 0.1	0.4	0.3	0.3
Potassium	2	< 1	< 1	1.8	< 1	< 1	1.1	< 1	< 1	3	< 1	< 1
Sodium	8	< 1	< 1	2	< 1	< 1	1.5	< 1	< 1	4	< 1	< 1
Aluminum	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Chromium	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Iron	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Copper	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Zinc	< 1	< 1	< 1	< 1	< 1	< 1	1	< 1	< 1	1	< 1	< 1
Lead	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Nickel	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1

Table 2 : Ionic extractables from polypropylene and polyethylene (in ppb)

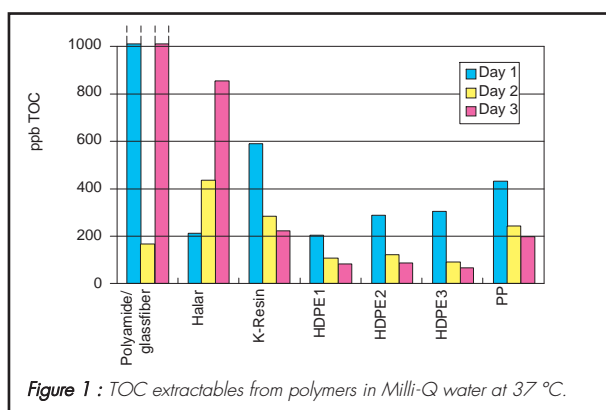


Figure 1 : TOC extractables from polymers in Milli-Q water at 37 °C.

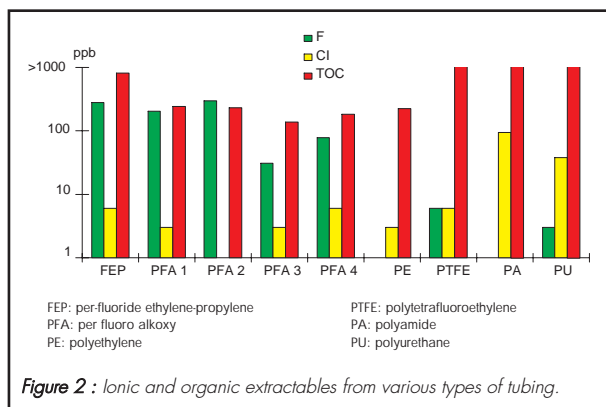


Figure 2 : Ionic and organic extractables from various types of tubing.

However, higher levels of Cl^- , NO_3^- , SO_3^{2-} and Mg^{2+} were present after the third day of extraction in polypropylene than in the various forms of polyethylene.

The high density polyethylene 2 displayed slightly lower extractable levels than the polyethylene 1 and 3 grades over a three day period. (See table 2). The release of organics was measured as ppb TOC.

Polyamide and Halar® show high levels of organic extractables. The decreasing TOC levels seen with polyethylene pellets indicate a more efficient rinse out than in other polymers (figure 1).

The combination of low levels of ionic leaching plus a faster organic rinsing step indicate that polyethylene grade 2 or 3 should be chosen as the material of construction for purified water storage reservoirs.

Additionally, all other parts of the water purification system undergo similar selection tests.

For example, figure 2 shows some extractable results from different plastic tubings in contact with ultrapure water at 37 °C for 7 days.

To transfer water from the storage reservoir to the final polishing water purification system, data suggest the use of polyethylene tubing is preferential to other materials tested.

Storage Reservoir Design

Selection of the best process for reservoir production. The physical contours and the surface quality affect the overall cleanliness of the reservoir. Biofilm, the adhesion and accumulation of microbes on the wetted surfaces of the reservoir, is a chronic contamination problem⁸. Smooth surfaces reduce biofilm formation and subsequent microbial problems.

Both blow molding and rotomolding results vary with the polymer material being used. SEM images were taken of the inner surface of a polypropylene and a polyethylene storage reservoir. There was a clear difference in surface characteristics; polypropylene showed roughness and crevices which may result in microscopic stagnation (figure 3).

Rotomolding is a common production process which tends to give the interior reservoir wall a rough

surface. In contrast, blow molding produces a smooth surface with regular polymer composition, thinner walls and a lighter weight reservoir.

A Scanning Electron Microscope and Zygo's NewView 100 Scanning White Light Interferometer were used to perform surface analysis on reservoir inner walls.

The surface quality of blow molding versus rotomolding was clearly seen in interferometer results. *Figures 4 and 5* show average roughness and peak to valley values, a line graph, a spectral display and a "y- modulated 3-D" oblique plot.

Considering the surface roughness obtained in each case, more than a 24 μm variation was obtained with rotomolding while less than 14 μm variation was

seen using the blow molding technology. The correct production technique, blow molding as well as the best polyethylene raw material result in a reservoir suitable for storing purified water.

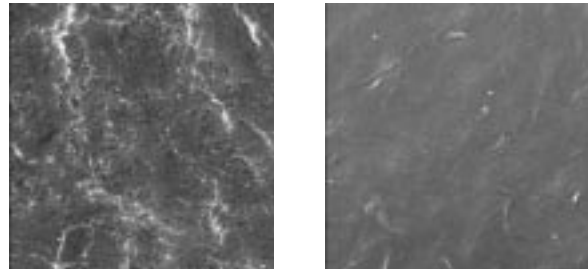


Figure 3 : SEM images of Polypropylene (left) and Polyethylene (right) Surface (40X).

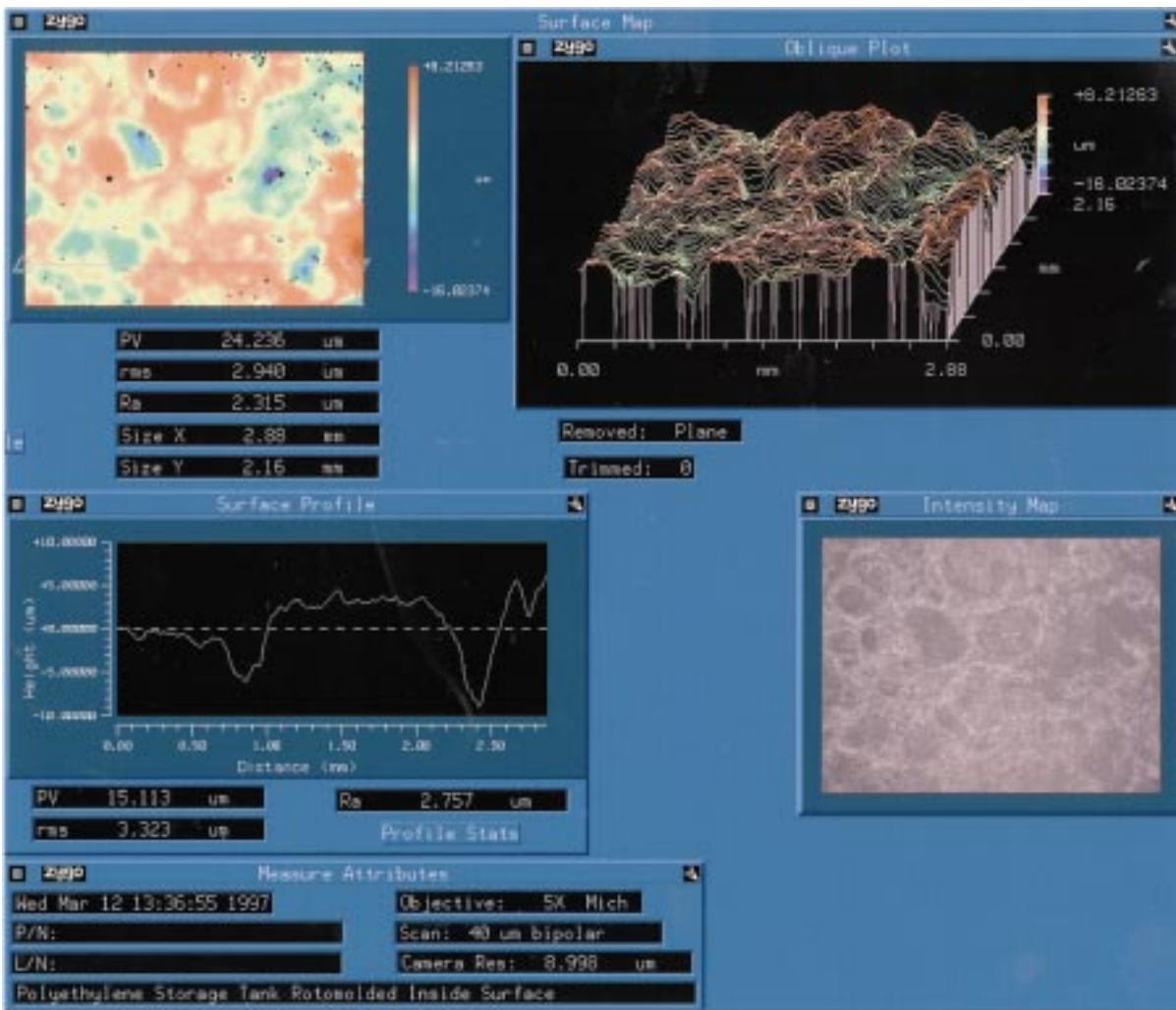
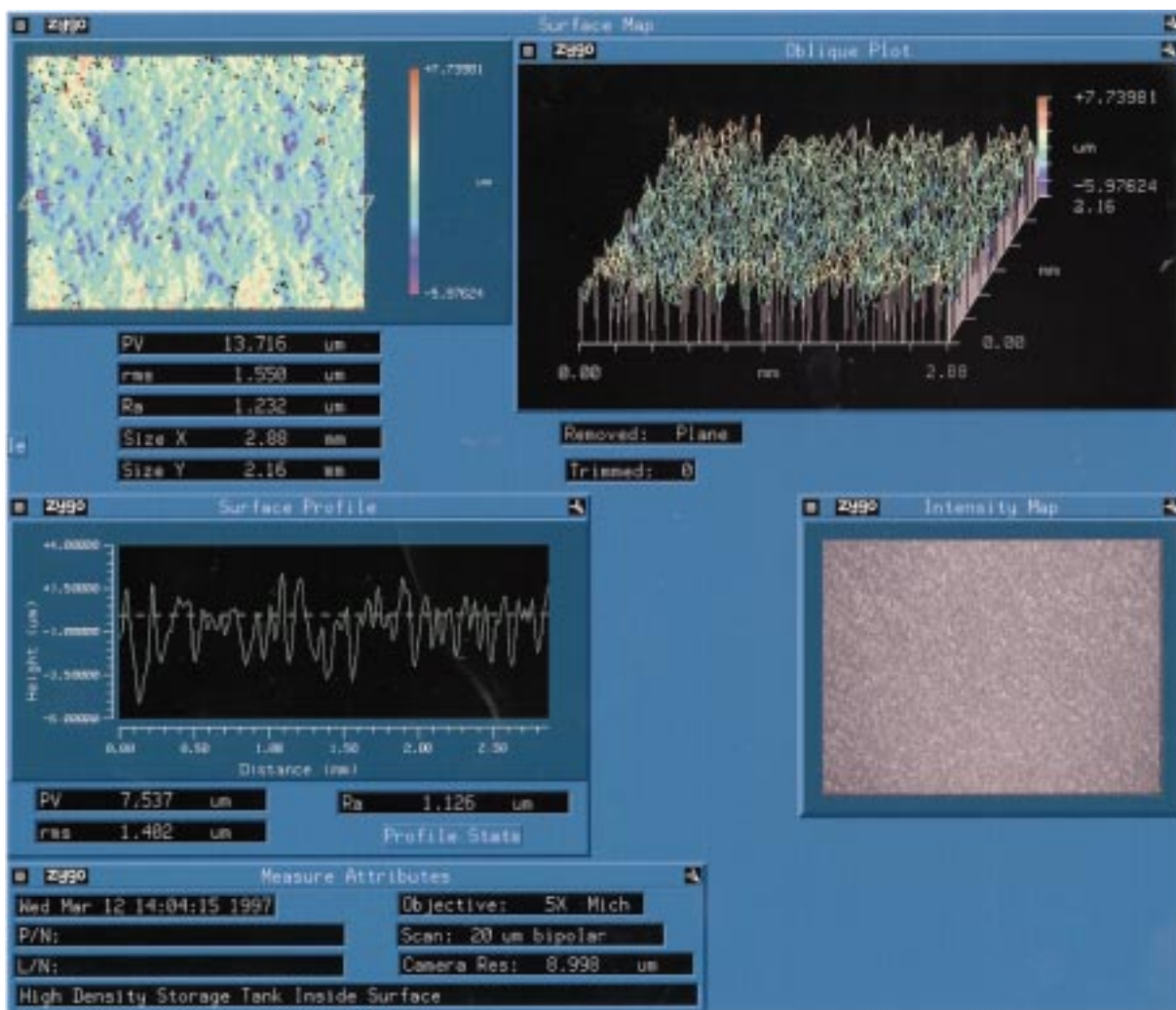


Figure 4 : Rotomolded polyethylene tank inner surface studied by Zygo's NewView 100 Scanning White Light Interferometer

Microscopic studies performed by Robin de la Parra, Millipore Corp., Bedford



Microscopic studies performed by Robin de la Parra, Millipore Corp., Bedford

Figure 5 : Blow molded polyethylene tank inner surface studied by Zygo's NewView 100 Scanning White Light Interferometer

Air-vent

Need and Purpose of an Air Vent

One major source of external contamination is from air entering the storage system. When a given volume of water is used from the storage reservoir, the water level in the reservoir decreases and is replaced by an equivalent volume of air. Storage reservoirs require vent filters to equalize the reservoir pressure with that of the atmosphere when liquid is added or withdrawn.

The laboratory atmosphere contains carbon dioxide gas (CO₂) and some volatile organics. When CO₂ dissolves in water, carbonic acid is produced which dissociates to yield bicarbonate and hydrogen ions. The reaction increases the ionic content of the pure water and subsequently increases the challenge to ion exchange resins used in polishing systems. Millipore has developed a unique vent filter which significantly reduces atmospheric organic and ionic contamination entering the reservoir.

Structure and features

To protect the stored water from external, air-borne contaminants, the vent filter device must be hydrophobic and adsorb or retain volatile organics, CO₂ and particles. The vent device, as shown in figure 8, contains a 0.65 μm hydrophobic filter, activated carbon and soda lime. Soda lime absorbs 25-35 % its weight of CO₂.

Selection of air-vent raw materials

Each component of the vent was tested for effectiveness under laboratory conditions. The membrane filter must exhibit a low pressure drop to allow proper filling and draining of the reservoir. Therefore, a 0.65 μm hydrophobic Durapore™ membrane was selected. It also provided an efficient retention rate for particle and bacteria removal.

Retention studies of volatile organic solvents were performed on different activated carbon types using the test bench described in figure 6.

Three different types of activated carbon were evaluated for their retention of acetone and toluene. In the case of toluene, the ultrapure water was substituted with 200 ml of ethanol (spectroscopy grade) in the final collection flask.

The presence of organic solvents in the collection flask solution was detected by monitoring the UV absorbance (optical density).

As shown in figure 7, the acetone retention capacity of activated carbon C was approximately two times higher than that of activated carbon A and three times higher than that of activated carbon B.

For toluene, the corresponding values were around 1.5 and 2.5 times. Consequently, activated carbon C was selected for use in the air vent device.

Experimental data show that over 3000 m³ of air containing 1.8 mg/m³ acetone (the maximum human exposure limit) can pass through the vent without acetone release. In air containing toluene at the exposure limit of 375 mg/m³, the air throughput capacity was lower at 20 m³. These capacity figures are compatible with regular maintenance on water purification system expendables.

A final validation of the vent filter was performed by placing vent filters on 30 liter reservoirs fed by Elix™* water purification systems. The results were compared to those of reservoirs with vent filters without activated carbon. A pump placed at the reservoir outlet was programmed to empty the reservoirs automatically for 30 minutes during a normal 8 hour working day. TOC at the reservoir outlet was monitored via an Anatel A100P TOC analyzer. To introduce contaminated air, the vent filter was connected to a second 30 liter reservoir containing air contaminated with toluene vapor. Addition of toluene into this second air-filled reservoir produced volatile organic TOC concentrations up to 7050 ppm.

Table 3 shows the TOC levels for the reservoirs with and without activated carbon in the vent filter. After reaching equilibrium, a 60 to 100 times lower TOC level was measured in water stored using the vent filter containing activated carbon versus water stored with the vent filter without activated carbon.

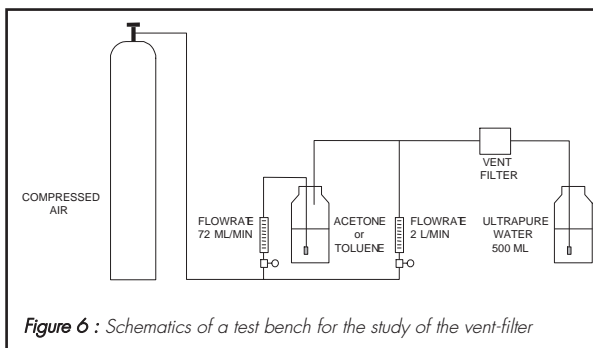


Figure 6 : Schematics of a test bench for the study of the vent-filter

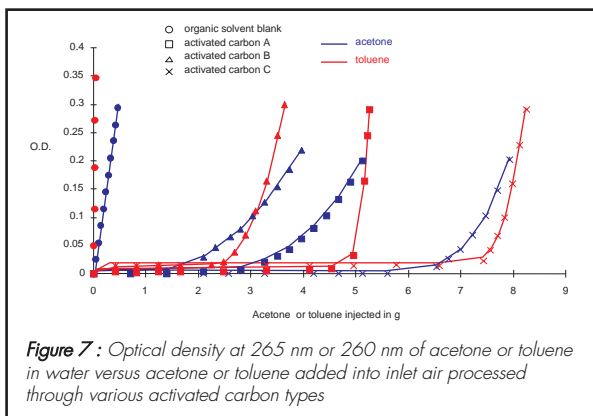


Figure 7 : Optical density at 265 nm or 260 nm of acetone or toluene in water versus acetone or toluene added into inlet air processed through various activated carbon types

cumulated ELIX water stored in liters	Stored water TOC (ppb) No activated carbon	Stored water TOC (ppb) activated carbon
30	45.3	14
60	751	12
90	668	10
120	553	11
150	492	9
180	749	9
210	582	8
240	484	8
270	794	9
330	800	7
360	611	8
390	464	7

Table 3 : Effect of activated carbon in vent cartridge on stored water TOC level (in ppb)

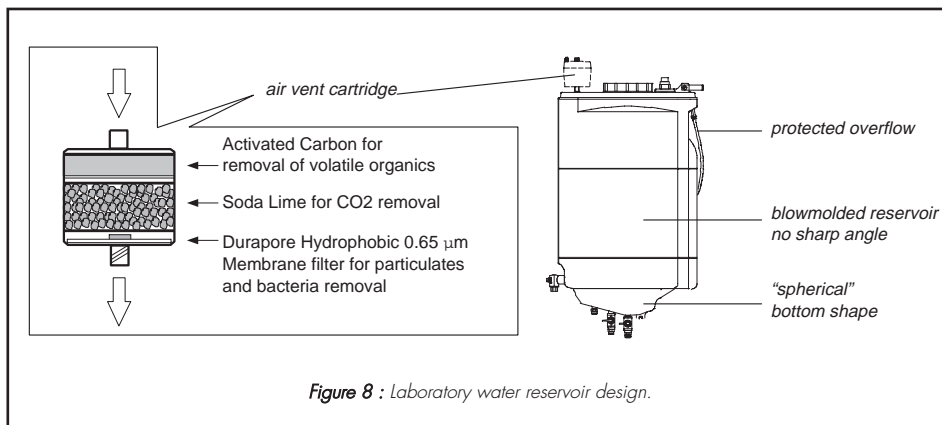


Figure 8 : Laboratory water reservoir design.

The activated carbon in the vent filter was clearly effective in protecting purified water from an environment contaminated with high concentrations of volatile organics.

Additional tests were performed to measure the TOC and the resistivity of the stored water. This experiment was performed on a larger reservoir size.

A 60 liter reservoir was fed by an Elix 10 system. Filling and draining periods were controlled automatically. The vent filter, placed on top of the storage reservoir, contained soda lime, activated carbon and 0.65 μm membrane filter (figure 8).

Yokogawa resistivity meters equipped with Millipore 0.01 cm^{-1} cell constant sensors measured reservoir inlet and outlet resistivity. An Anatel A-100 P measured reservoir TOC at the inlet and outlet.

Prior to the experiment, the storage reservoir was filled and emptied twice before starting any measurement.

Figure 9 shows the typical TOC and resistivity of Elix quality water stored in the reservoir during regular daily use.

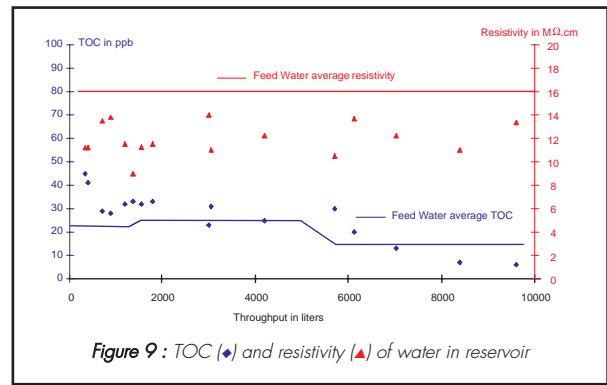


Figure 9 : TOC (♦) and resistivity (▲) of water in reservoir

With the use of the activated carbon-containing air vent, low levels of TOC and high resistivity are achieved.

The reduction of organic levels in the purified water helped reduce bacterial growth. However, storing high purity water for extended periods may still lead to biofilm formation. Thus, additional antimicrobial measures may be required to eliminate bacterial growth.

Bacterial contamination

Water system users commonly associate water storage vessels with bacterial proliferation. As mentioned earlier, biofilm, although reduced by smooth and inert surfaces, may still grow slowly on the walls of the reservoir. UV radiation has been proven effective in countering bacterial proliferation.

Various flow and placement configurations were considered to optimize the effectiveness of UV bacterial sanitization. For example, recirculation of the water through a UV lamp placed outside the reservoir resulted in a slight temperature increase. This created condensation droplets on the inner surface at the top of the reservoir creating a source for contamination. The best result was obtained by placing the UV lamp inside the storage reservoir.

Optimal UV lamp cycle time was tested by examining resulting bacterial reduction and considering lamp intensity and UV penetration in water. Figure 10 represents the UV lamp luminous flux as a function of the distance from the light source. Although the flux decreases quickly, the energy required to kill bacteria was around 10 mW/cm^2 . This means that 10 cm from the UV lamp, 5 minutes of 2 mW/cm^2 exposure was sufficient to deliver a bactericidal dosage of UV (at 254 nm). The lamp can operate up to 60 minutes per day and thus destroy bacteria in the total volume of the reservoir.

To demonstrate the efficiency of the automatic UV sanitization module, two reservoirs were fed by a single reverse osmosis water purification system which had intentionally not received regular sanitization.

One reservoir was equipped with the UV lamp; the second one was not. Fifty liters were drained from the reservoirs at the end of each afternoon. Then the reservoirs were filled again for 4 hours before 50 liters more were dispensed to drain. Freshly produced water filled automatically overnight, and after a steady state period of 6 hours, sampling was done. Total bacteria assays were done using the MilliFlex™ system with pre-filled agarose gel cassettes.

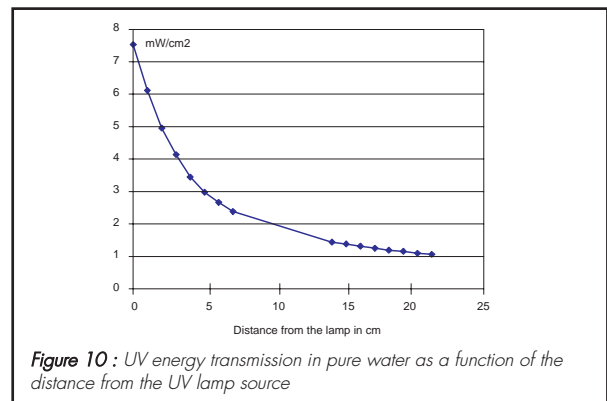


Figure 10 : UV energy transmission in pure water as a function of the distance from the UV lamp source

Results are shown in *figure 11*.

The bars represent bacteria levels (in cfu/ml) in the storage reservoirs.

After 15 days, contamination over 350 cfu/ml can be seen in the reservoir without the UV lamp (blue bars). However, no growth appears in the reservoir equipped with the automatic sanitization system (red bars).

After 30 days, the UV lamp from the first reservoir was placed in the contaminated storage reservoir. A dramatic decrease of the contamination level can be seen. This new configuration was observed for 12 days, after which the initial configuration was replaced.

During the third stage of the experiment, a small contamination increase in the tank equipped with the UV lamp can be seen between day 42 to 53. During this period, the UV lamp was on 5 minutes per hour. After 55 cycles, 10 minutes per hour was chosen for the UV illumination period. By using 10 minute UV exposures, the previous non-contaminated level was finally achieved.

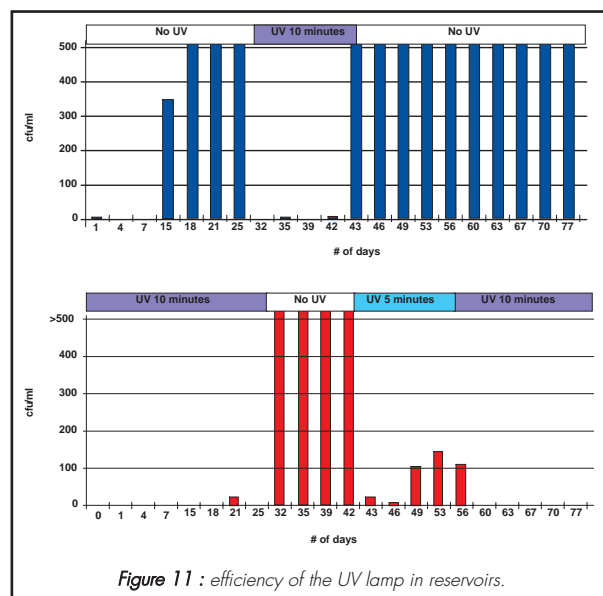


Figure 11 : efficiency of the UV lamp in reservoirs.

The 254 nm UV lamp is thus a valid solution for preventing the formation of biofilm on inner reservoir surfaces.

Conclusion

Contamination of high purity water during storage has proven to be a challenge for those doing ionic or organic analyses. Previous studies indicate that the quality of purified water degrades with storage time.

An on-demand water purification system must have the ability to supply the water volume needed. The storage reservoir allows the delivery of required water volumes in periods of either low or high demand. It also enables on-demand feed of an ultrapure water purification system.

With carefully selected raw materials, an optimized air-vent filter, and a bacteriocidal UV lamp, it is possible to maintain high quality purified water during storage.

Acquiring a storage tank which has undergone the various selections and tests described in the present paper offers a way of storing high purity water in optimal conditions. Moreover, this equipment helps maintain the integrity of the entire downstream ultrapure water system.

*ELIX™ systems are water purification systems which combine reverse osmosis and electrodeionization.

References

- ¹ "Detection and characterization of organics in semiconductor DI water processes" Ven Anantharaman, Bipin Parekh and Ramesh Hegde, *Ultrapure Water* 11 (3), pp 30-36 (1994)
- ² "Degradation of High Purity Water on Storage" Raymond Gabler, Ramesh Hegde and David Hughes, *Journal of liquid Chromatography* 6 (13), pp: 2565-2570 (1983)
- ³ "Trace Metal Assessment of Lake Michigan Tributaries Using Low-level Techniques" James P. Hurley, Martin M. Shafer, Susan E. Cowell, J.T. Overdier, Peter E. Hughes and David E. Armstrong, *Environ. Sci. Technol.* 30 (6), pp: 2093-2098 (1996).
- ⁴ "Effects of water quality on in vitro fertilization and development of bovine oocytes in protein-free medium" Y. Nagao, K. Saeki, M. Hoshi, Y. Takahashi and H. Kanagawa, *Theriogenology* 44, pp 433-444 (1995)
- ⁵ "The effect of water quality on the electrical characteristics of Langmuir monolayers" D.M. Taylor, O.N. Oliveira, Jr., and H. Morgan, *Thin Solid Films*. 173 pp L141-L147 (1989)
- ⁶ "Leaching of organotin compounds from poly(vinylchloride) (PVC) material". Ph Quevauviller, A. Bruchet and O F X Donard, *Applied Organometallic Chemistry*, 5, pp 125-129 (1991)
- ⁷ "Leach-out Test Method for Ultrapure Water Piping Materials". Working group for Clean Room, UC Standardization Committee, March 1996 UC standard pp 355 - 363 (1996)
- ⁸ "Bacterial growth and biofouling control in purified water systems" from *Biofouling and Bioconversion in Industrial Water Systems* M.W. Mittelmann - Springer-Verlag pp 133-154 (1990)