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Impact of feed water quality on the production of ultrapure water

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Abstract: *The quality of ultrapure water delivered by a water purification chain is often only monitored through resistivity measurements. The production of this ultrapure water requires several steps. When starting from municipal water, pretreatment has to be performed prior to the final polishing process.*

Among the initial possible purification technologies used are deionization or reverse osmosis/electrodeionization. Although both techniques can yield high resistivity final ultrapure water, significant differences may be observed when TOC values are also studied in order to monitor the ultrapure water quality more accurately. Higher TOC values are observed and more stringent maintenance operations are necessary when choosing DI pretreatment.

Moreover, purifying water through regenerated resin beds may lead to organic release onto the ion exchange polishing media and the final filter, impairing the efficiency, reliability and lifetime of the final purification consumables.

Introduction

Production of ultrapure water is achieved through a combination of purification technologies. Each step is optimized in order to remove different kinds of impurities, including the most specific ones.

The water purification chain can be divided into three units; the initial purification system, the storage reservoir and the final polishing system. The initial purification system produces purified water from well or municipal water. During this step, deionization, distillation or reverse osmosis technologies can be used. Distillation successfully eliminates most types of contaminants. However, it is energy consuming and the low flow rate requires the use of a storage reservoir that is not always adapted to maintaining the water quality. Deionization seems the simplest and cheapest method in terms of investment, but the water quality is not

stable as fluctuations occur when resin is saturated. This process is mainly dedicated to ion removal, with low impact on other contaminants such as organics and particles. Both these water purification techniques can provide good enough water quality for many applications provided the final polisher eliminates residual trace contaminants for more critical water quality requirements.

However, poor purification at the initial purification stage, not only leads to water quality problems at the final polishing step, but also shortens the lifetime of the polishing cartridges.

In this study, the impact of different initial pretreatment methods on the quality of the ultrapure water produced is shown. The influence of residual contaminants on different purification components is analyzed.

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Experimental

Water purification chain

Two final polishing systems, Milli-Q Academic (Millipore), are fed by municipal water (Mita, Tokyo) purified via two different pretreatment systems (as shown in figure 1):

- System A is fed with water purified by a deionization cartridge (5 liter volume of mixed bed resins). The deionization cartridge is replaced by regenerated resin when the water resistivity drops to less than 1 Mohm.cm.
- System B is fed with water purified through a combination of reverse osmosis and electrodeionization technologies, Elix 10 (Millipore), kept in a 60 liter storage reservoir.

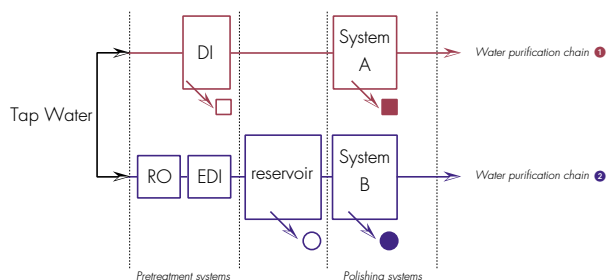


Figure 1: Water purification chain schematics.

Method

Flow rates are adjusted at 1.5 liters per minute. For 60 liters of daily water dispense, resistivity and TOC are measured by a A-100P SE TOC monitor (AnateI®) for each system. Feed water TOC is also monitored. The different water sampling points are indicated in figure 1.

Results and discussion

As the results in figure 2 show, the resistivity of DI water, as expected, is initially high at 18 Mohm.cm. However, after processing 500 liters, a significant drop in resistivity can be seen and replacement of the DI cartridges, in this case, does not allow the recovery of this high resistivity value, the maximum reached being around 15 Mohm.cm. This indicates that DI water quality may vary quite significantly due to the regeneration process. The system combining reverse osmosis and electrodeionization technologies, on the other hand, produces 15 Mohm.cm water consistently. Due to a low flow rate, this water has to be stored in a reservoir before feeding the final polishing system. This leads to a

drop in resistivity, mainly due to carbon dioxide. An optimized reservoir¹ allows the purified water to be maintained at around 2 to 6 Mohm.cm as indicated in figure 2. Moreover, the same water quality is delivered throughout the whole experiment without the need for resin regeneration. However, for both feed water types, the resistivity of the water delivered by the final polishing system (A or B) reaches 18 Mohm.cm.

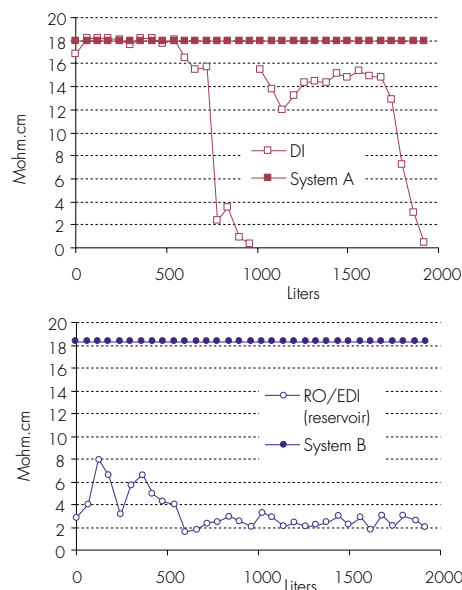


Figure 2: Resistivity obtained for DI water and system A (top) and RO/EDI water and system B (bottom).

Although both water purification chains give good results in terms of ion purification, significant differences are to be noted in TOC quality. First of all, when produced through DI resin beds, there is a huge variability in the feed water TOC. As seen in figure 3, DI purified water can show unstable TOC values fluctuating between 100 and 550 ppb. When newly regenerated resin beds are installed, high TOC values of up to 640 ppb may occur. On the other hand, the water purified through the Elix system, combining RO and EDI technologies, shows TOC values mostly under 50 ppb, even after storage in the reservoir for more than one night. The feed water to the final polishing system is, in this latter case, of more consistent quality than that of the DI cartridges. As a result, significant differences in terms of TOC water quality are noticed in the final ultrapure water produced. Figure 4 indicates TOC variations in the ultrapure water produced by the final polishing system A or B. System A has higher TOC than System B throughout the experiment.

System A, DI feed, has high and fluctuating TOC levels between 50 ppb and 150 ppb. System B, Elix feed, shows TOC concentrations constantly around 10 ppb. The higher initial value, corresponding to the very first distribution of water of the day, is due to overnight accumulation of organics. Once the

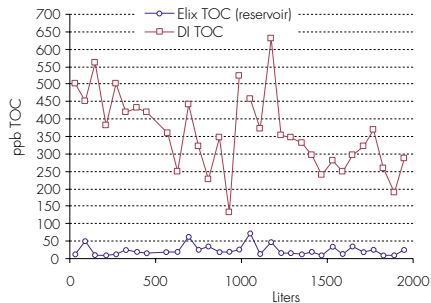


Figure 3: Feed water TOC comparison.

ultrapure water is distributed, consistent good quality water (18.2 MΩ.cm and <10 ppb TOC) is obtained. This clearly shows the advantage of using an Elix type system combining reverse osmosis and electrodeionization as pretreatment.

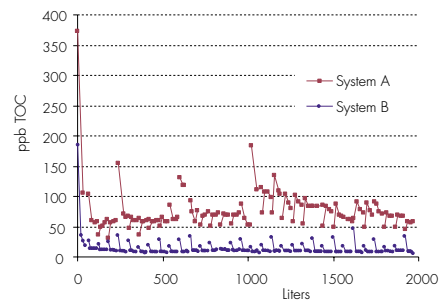


Figure 4: Ultrapure water TOC comparison.

Part II : The influence of the initial water purification technology on the ion exchange resin and the membrane filter installed in the final polishing system.

Experimental

For this experiment, two Milli-Q systems are fed by water pretreated through two different techniques: reverse osmosis or deionization. The polishing cartridges are changed when resistivity drops (500L for DI feed system) or after 2000 liters of water have been processed (for RO feed system). At these points, the surface of the ion exchange resin of the purification pack and of the final membrane filter of the Milli-Q systems are observed using a S-510 scanning electron microscope (Hitachi). Samples are thoroughly dried and pretreated by gold sputtering for SEM analysis.

Results and discussion.

Figure 5 shows SEM images of anion exchange resin surface of a) new resin, b) resin fed with 2000 L of RO water c) resin fed with 500 L of DI water. The micro-structure of the surface of the resin fed by RO is similar to that of new resin. The structure of the DI fed resin, however, is not easily observable and the

surface is completely covered by fouling substances or particles. Organic or colloidal substances seem to be coating the resin surface. This phenomenon is not only due to the ion exchange process but follows an adsorption mechanism on the bead surface. Even though some charged matter might be ion-exchanged by the resin, limitation by size, molecular weight or polarity prevents the contaminants from diffusing inside the resin structure. Thus, surface fouling occurs and the resulting interference on the ionic transport yields slower ion exchange kinetics and induces water quality defects such as resistivity drops. Sometimes, the lifetime of ion exchange resin can be shortened by this phenomenon even though the resin might not be saturated and good ionic quality feed water is used. This coating is not observed on the surface of the cation exchange resin. This indicates that the contaminants are negatively charged substances such as regular organic and colloidal substances found in natural water².

Figure 5: SEM images of anion exchange resin surface from purification pack of Milli-Q system



Figure 5a: new anion exchange resin.

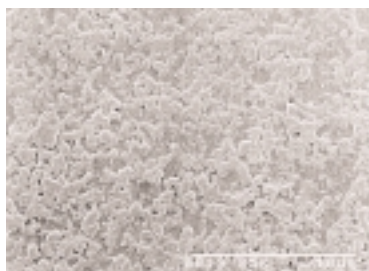


Figure 5b: anion exchange resin fed by 2000 L of RO water.

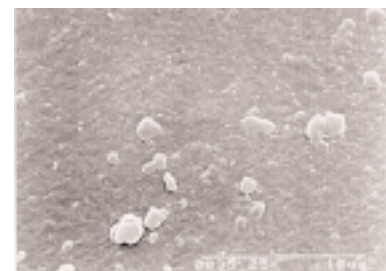


Figure 5c: anion exchange resin fed by 500 L of DI water.

Figure 6 shows the membrane surface of the final filter. In Figure 6a, RO feed system, the membrane pore structure is well recognized by the SEM image and nothing is observed on the filter other than several small particles. In the DI feed system image, the membrane surface is completely plugged by matter as shown in Figure 6b. A cracked coated layer on the membrane surface is clearly observed

after the drying step. This indicates that organic or colloidal substances, not efficiently removed by the DI purification technology, plug the final filter of the downstream water purification system. This will limit the final production flow rate by the resulting pressure drop, and the significant organic material present will increase bacterial growth and enhance biofilm formation.

Figure 6: SEM images of final filter

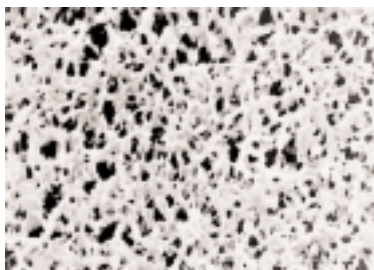


Figure 6a: Milli-Q system fed by 2000 L of RO water.

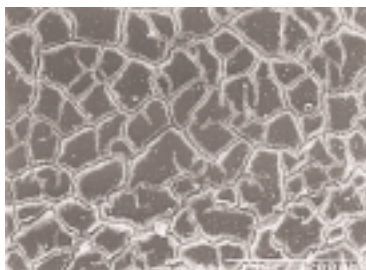


Figure 6b: Milli-Q system fed by 500 L of DI water.

Conclusion

A combination of technologies is mandatory in the production of ultrapure water. Although resistivity is an efficient way to monitor the ionic quality of ultrapure water at different purification steps, other contaminant types not measured by resistivity, such as organics, may significantly impact the success and reliability of experiments⁴. This impact can be easily highlighted when comparing the performance of an ultrapure water system fed with different pretreated water qualities.

Both the DI process and the association of reverse osmosis and electrodeionization produce water with good resistivity for a final polishing system. The resulting ultrapure water shows high resistivity in both cases, but significant discrepancies are noticed as far as TOC levels are concerned. This is due to the high

variability of the organic content of purified water through the DI process where regenerated resin media is used. And this poor organic purification in the pretreatment phase may lead to coating of the anion exchange resin in the final polishing systems. This will induce early media completion and might produce plugging of the final filter.

When producing ultrapure water for laboratory applications, it is highly recommended that RO/EDI pretreated water be chosen rather than DI water to feed polishing systems. This minimizes TOC variability in the feed water and ensures consistent ionic and organic quality water. In order to check that the resulting ultrapure water quality is suited to all laboratory applications, it is also important to monitor TOC levels as well as resistivity at the point of use⁵.

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