

Sources of TOC in Deionized Water

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Keywords:

Summary: Sources of TOC in water can be from man-made or “natural” organic matter (NOM) present in the raw feed-water, or can be caused by leachables from ion exchange resins. In the case of NOMs, the ionized portion can be readily removed by anion ion exchange resins. Manmade organics are removed by ion exchange only if they are ionized. In ultra-pure water systems, the organic removal resin should be separate from the deionized resin to avoid the consequence of organic fouling. The best candidates for organic traps are acrylic strong based anion resins and styrenic resins with high gel phase porosity.

In ultra-pure water systems, leachables coming from the resins themselves are important. New resins used in ultra-pure water applications require vigorous cleaning to remove leachables. The key to any system design that requires low TOC is to understand the nature of the organics that are present in the feedwater and then to select appropriate equipment technologies for their removal

INTRODUCTION

The purpose of this paper is to explore what the term “organics” means when used in context with water treatment and to describe the relationship between the presence of “organics” and ion exchange.

Thirty years ago, ultra-pure water was determined by conductivity or (resistivity) alone, both in the microelectronics industry and in the power industry. Only the pharmaceutical industry was interested in the organic content of the treated water.

If any attention was paid to the organic content of water in other industries, it was usually due to the concern of organic fouling of the anion resin component in the deionization system.

Methods of determining organic content at that time were rather crude and indirect. The pharmaceutical industry used a nitrogen or nitrogenous matter test while other industries used chlorine demand, oxygen demand, and/or permanganate demand.

USP Standard	Water For Injection (pre 1998)	Water For Injection (1998)
TOC limit ppb	None	500

SEMI Guidelines	1989	1992
ppb TOC Attainable	20	<1
ppb TOC Acceptable	50	<2
ppb TOC Alert	100	5
ppb TOC Critical	400	10

	ASTM D-1193 (1983)	ASTM D-1193 (1991)	ASTM D-5127 (1990)
Grade Water	Reagent Grade I	Reagent Grade 1	Electronic Type E-1
TOC limit Ppb	None	100	25
KmnO4 Retention minutes	60		

TOC in DI

Today, the organic content of water is important to many industries. The preferred method of describing organic content has become the Total Organic Carbon (TOC) measurement. This measurement has replaced most of the earlier, less direct methods of measuring organic content. TOC is a (relatively) simple test that (more) directly measures the organic content of water. However, as of 1998, the available methods to measure TOC do not recover 100% of all organic matter that might be present.

TOC measurements will always be somewhat limited because they only describe concentration and don't tell us anything about the chemical structure of the organics. Future requirements for ultra-pure water will almost undoubtedly necessitate even more accurate methods of determining both the structure, as well as the concentration of organic matter that may be present.

The concern about organic content varies widely from industry to industry. For example, the pharmaceutical industry has adopted a new standard of 500 ppb of TOC for "Water for Injection." The boiler industry has a maximum standard of 25-50 ppb TOC for high-pressure boilers to prevent corrosion caused by organic chlorides and sulfates. The microelectronics industry has a minimum standard of no more than 10 ppb of TOC.

Most state-of-the-art ultra-pure water systems expect 1 or 2 ppb; some hope to produce under 1 ppb of TOC. Since low TOC in one industry may be 500 times what low TOC in another industry means and the reasons for removing TOC are not always the same, the differences must be defined in any discussion about the subject.

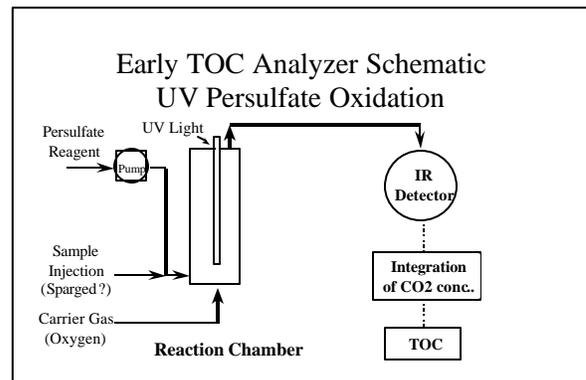
The term TOC or Total Organic Carbon, refers to a direct or indirect method of measuring the concentration of carbon present in a water supply, and excluding the inorganic forms of alkalinity (CO_2 , HCO_3^- , CO_3^{2-}).

In relatively high TDS water supplies, TOC is generally measured by U.V. persulfate oxidation and I.R. detection of carbon dioxide. Inorganic carbon is removed by acidification and gas stripping. The remaining organic carbon then reacts with an oxidant (in the presence of a catalyst). The organic carbon is converted to carbon dioxide, which is removed by a carrier

gas. The concentration of carbon dioxide created from the organics is then determined by infrared detection.

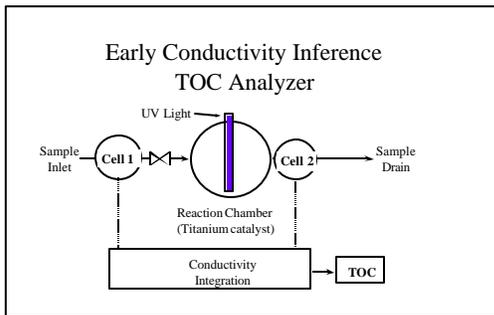
In order to perform this analysis, the initial inorganic carbon content (large, compared to the organic content) must first be removed. This is generally done by purging the sample with oxygen. Solvents and other purgable organics are lost during this sample preparation step. In addition, some forms of organics are difficult or impossible to oxidize. The oxidation method of determining organic carbon does not always result in 100% recovery of the total organic carbon present.

Another method of measuring TOC involves a less direct approach and is limited to low conductivity water. Organic carbon is oxidized in the presence of UV light and an electrical and/or metallic catalyst. The increase in conductivity due to formation of carbon dioxide is used to calculate the concentration of carbon dioxide produced in the analyzer.



This method has its own unique advantages and disadvantages. The conductivity method is limited to relatively low T.D.S. waters and is at its best in ultra-pure water. Since many organic compounds contain ions other than carbon, hydrogen and oxygen, (such as, chlorine, nitrogen, phosphorous and sulfur), the conductivity measurement can be distorted by the presence of inorganic acids created during the oxidation step. Various methods are used to minimize this distortion. Another problem with TOC analyzers that use conductivity inference is that many ultra-pure waters today have low oxygen contents. Since the oxidation reaction requires oxygen to convert the organic carbon to carbon dioxide, the analysis of low levels of

TOC in deoxygenated water by this type of device is questionable.



Part 1 - Raw Water Organics

The goal of this paper is to put organics into perspective with respect to their relationship between ion exchange resin and process requirements. Naturally, the place to start is the raw water, with a brief discussion about what organics are.

The text book definition of organics includes all compounds that contain carbon, except certain simple compounds designated as inorganic carbon. The distinction is made somewhat arbitrarily and there are exceptions to every definition. For instance, some amines (nitrogen compounds) contain no carbon at all and yet are considered organic. "Inorganic" carbon dioxide in some cases is clearly derived from decomposition of larger organics and belongs in the organic grouping. TOC is truly an example of this. Rather than defining organic compounds by the classical methods, from our standpoint, it is easier to define them as natural organic matter (NOM) or man-made; and further to classify them as ionized or non-ionized.

Most naturally occurring organic matter falls into the broad category of large carboxylic acids; primarily tannic acid and humic acid. Man-made organics cover a much broader grouping. Many man-made organics are purified by ion exchange. Two of the largest applications are that of sugar refining and the production of MTBE for use in gasoline. However, in the world of ion exchange, we are generally concerned with either the removal of organics and/or the consequence of organic fouling of the ion exchange resins.

With respect to removal, it is important to remember that ion exchange materials only

remove ionized forms of organics. Non-ionized organics (including many, if not most of the man-made organics) are generally not removed to any significant extent by ion exchange processes. This is one reason (among many), that most ultra-pure water systems include membrane processes, as well as ion exchange.

MOMs – Manmade Organic Matter

In any discussion about the affect of man-made organics on ion exchange resins, it is necessary to have some knowledge about the basic chemical functional groups. The TOC concentration by itself, is of very little value. For instance, amines are cationic and are removed by cation exchange, organic acids are partially ionized anions and are partially removed by anion resin, while sugars are non-ionized and are not removed by ion exchange.

Ionized man-made organics are generally well removed by ion exchange resins; sometimes, too well removed. Certain classes of man-made organics, such as alkylsulfonates and benzene sulfonates, are so strongly exchanged by anion resins that they poison the resin and irreversibly foul it. Other groups of man-made organics undergo chemical reactions in the presence of ion exchange resins. Ion exchange resins are used in a number of organic synthesis reactions and as catalysts. Certain classes of organics, such as sugars, glycols and alcohols have little or no effect on resins, but resins are used to purify them during their production.

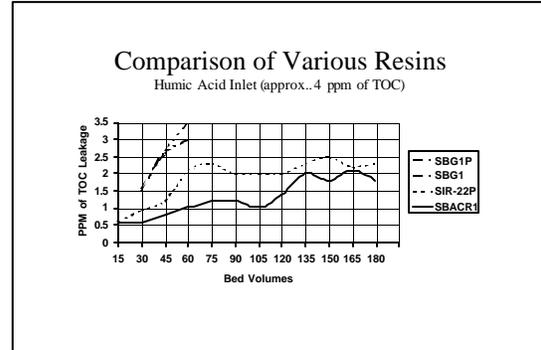
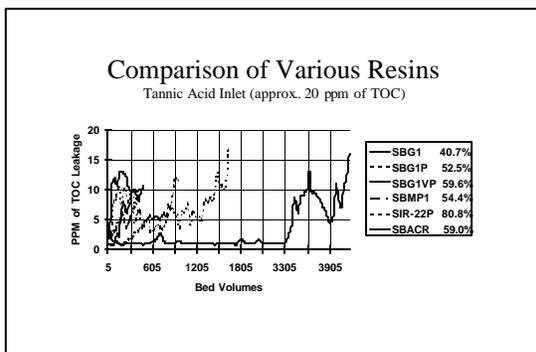
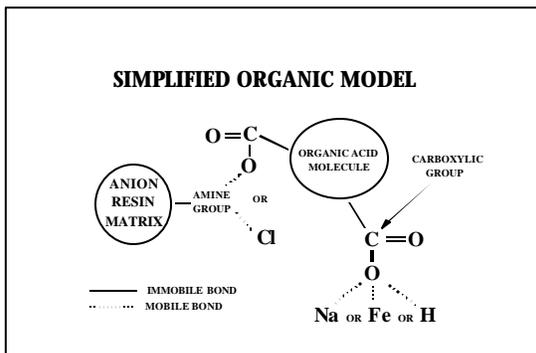
Man-made organics that are not ionized present a more difficult challenge in the design of ultra-pure water systems that require low TOC. Simple low molecular weight organics (having fewer than 6 carbon atoms) such as alcohols, aldehydes and solvents do not damage ion exchange resin. Indeed, ion exchange resin can be used in the purification of these chemicals. However, low molecular weight non-ionized organics are not removed by ion exchange resin. Unfortunately, low molecular weight organics are not readily removed by granular activated carbon or by membrane processes. At present, there is no truly satisfactory method of removing these types of organics, although there are some recently developed absorbent materials that show promise for removal of simpler organic contaminants. Higher molecular weight non-ionized organics (having more than 6 carbon

atoms), are usually absorbable by granular carbon and are well rejected by reverse osmosis membranes.

Part 2 – Removal of NOMs

Fortunately, most water supplies do not contain high concentrations of man-made organics. The

main concern with respect to ultra-pure water is the removal of naturally occurring organics. Naturally occurring organics are generally composed of tannins and humic material from decaying vegetation. Their molecular weight varies tremendously on a geographical basis, and their structure is not well defined. However, they share a common trait in that the majority are at least partially ionized and contain carboxylic acid functional groups. NOMs are, therefore, categorized by having a high fraction of carboxylic acid functionality. This means that they are anionic in nature and are exchangeable by anion resins.



There have been many papers presented concerning the natural organics. In this paper we will limit our discussion to a review of the key features with respect to removal of NOMs by anion exchange.

1. The natural organic materials have affinities for ion exchange resins similar to sulfate ion.
- 2a. NOMs have various molecular weights from as low as 100 to as high as 80,000. The higher molecular weight NOMs are usually not fully soluble in water.
- 2b. For the most part, organics with molecular weights greater than 10,000 are removed in potable water systems by means of coagulation and filtration.
- 2c. The behavior of the remaining organics with respect to ion exchange resin is governed by kinetics rather than equilibrium.
3. The presence of (large) organic ions on anion exchange resin interferes with the exchange of (smaller) inorganic ions by blocking surface exchange sites. This creates the kinetic impairment typically associated with organic fouling.
4. Carboxylic acids function as cation exchangers picking up sodium during the regeneration cycle. This phenomenon increases the sodium leakage out of the anion resin and is associated with the characteristic long rinse of organically fouled anion resins.

5. Natural organics are dominantly anionic in nature. A small portion is non-ionic. A small portion is also cationic.
6. Whatever polymer matrix is chosen for the polymer structure, it will always work best when the gel phase porosity is high. Increasing gel phase porosity always increases the mobility of the organic ions and improves kinetics.
7. The acrylic polymer matrix is proven to have superior transport properties over the styrenic matrix and is always a better choice from a kinetic standpoint. However, this does not always translate into the best choice of resin for an organic trap as other factors also play a role.
8. Increased surface area of a resin increases the number ion exchange sites available to transport ions from the surface of the resin to sites deeper within the polymer. Fine mesh resins will generally work better than coarse mesh resins. A macroporous resin will generally work better than a gel resin of the same gel phase porosity. However, most macroporous anion resins have lower gel phase porosity, macroporous resins often do not perform well in organic traps.
9. The balance between the elution of organics during regeneration and the loading of organics during the service cycle determines whether a resin will or will not ultimately fail. Failure is caused by one of two factors:
 - a. The resin no longer works because it has loaded an excessive amount of organic during the service cycle, and there is not sufficient time for the organic to exchange out of the resin during the regeneration cycle. This condition causes the surface exchange sites to be over crowded, reducing the available sites for exchange and creating the condition known as kinetic impairment.
 - b. The presence of excessive amounts of organics on a resin bead can lead to bio fouling organic acids and ions are generally good growth media for bio-organisms. The acrylic polymer supports bio-growths better than styrenic polymer and is, therefore, more prone to this type of fouling.
10. Whatever the design of the organic trap, the key to success is controlling the regeneration process to ensure that the organics are properly removed during regeneration. Periodic extended cleaning procedures can also be used to purge accumulated organics from the resin.
11. Organics are never completely removed from a resin in the period of time associated with typical regeneration processes. In systems that are designed to accommodate the presence of organics, some allowance must always be made for fouling.
12. Organic acids are more soluble at alkaline pH than at neutral pH. This means that during the service cycle, the removal will always be better when the pH is high. It also means that the removal of organics during regeneration is enhanced by increasing the pH of the regenerant solution.
13. Proper pre-treatment of the feedwater to an ion exchange system can prevent the high molecular weight fractions of NOMs from reaching the resin. Since these fractions are the most difficult to remove from the resin, their removal can dramatically enhance the performance of the resin downstream. Techniques for removing these organics include absorption by granular carbon, coagulation and filtration, and various membrane processes.
14. Choices for organic trap resins.
 - a) Acrylic

The acrylic resins are superior from the standpoint of the transport of organic ions into and out of the

polymer. They are ideally suited for large municipal installations. High moisture content and discreet porosity (macroporosity), are also helpful. These resins are ideal in plants where careful attention is placed on the proper loading and regeneration factors. Acrylic resins are not always the best choice for smaller systems where little or no attention is placed on the regeneration requirements and where alkaline brine cannot be used to elute the organics.

b) Very High-Moisture Gel Styrenic

These resins have good transport characteristics, compared to regular porosity gel resins. Their capacity is about half that of acrylic resins, but they do not have the tendency to foul out. They are virtually equal to acrylic resins with respect to tannic acid removal, but are significantly worse with the higher molecular weight humic acid based organics.

c) Macroporous Styrenic Resins

These resins have significantly increased surface area, which may make them good candidates for organic trap resin providing they have high gel phase porosity. The high degree of surface area makes up for the relatively poor gel phase transport properties. Macroporous resins may have superior physical strength over gel resins and may be more tolerant to harsh treatment by regeneration and other cleaning processes. Macroporous resins always function better when they have high gel-phase porosity, as well as discreet porosity.

15. The presence of sulfate in a feed water directly competes against the organic ions for exchange sites, thus the loading characteristics of any resin in an organic trap application depends on the sulfate content of the feed-water. As the sulfate concentration increases, the available capacity for organic removal

decreases. This phenomenon helps prevent resin from fouling, but limits its ability to remove organics effectively.

Section 3 - High-Purity, Low TOC Requirements

So far, in this paper, we have discussed the removal of organic ions by ion exchange resin, now we come to a different aspect of the subject. Since ion exchange resins are made from organic materials, there is opportunity for the resins themselves to leach organics into ultra-pure water. New resins can release part per million levels of organics. Even after cycling, the leaching of organics from ion exchange resins can create intolerably high levels of TOC in ultra-pure deionized water.

In the case of ultra-pure water, particularly that used for microelectronics manufacturing and wafer cleaning; the requirements for TOC are so stringent that the leaching of organics from ion exchange resins is a major cause of TOC in the final product water.

In the processing of ultra-pure water, the pretreatment stages; including membrane processes, often produce a feed-water to the final polishing demineralizers in the single digit ppb range of TOC. The UV TOC destruct lights further reduce the concentration of TOC such that the main concern with respect to the resins is that of leaching very low levels of TOC into the product water.

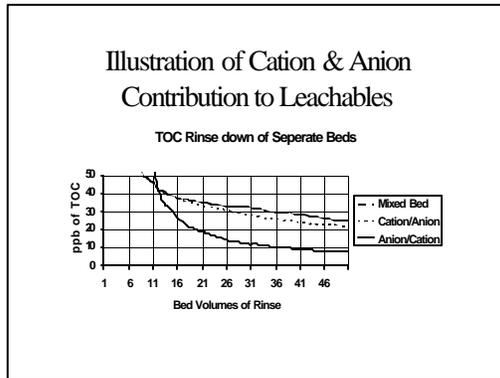
In cation resin the dominant leachables are sulfonated aromatic compounds. Their molecular weight depends on the cross-linkage and conditions of polymerization. The molecular weight and chemical structure of cation leachables is subject to some disagreement among polymer chemists. However, there is a clear relationship between the age of a cation resin and the concentration of organic sulfonate leaching off the resin. There are also differences among resins depending on the conditions of polymerization and with respect to the extent of post-treatment prior to use. Generally, their molecular weights are multiples of the benzene sulfate monomer.

Hydrogen form cation resins, if not very recently manufactured, usually bleed these organic sulfonates. These leachables increase the TOC level that the resin is otherwise capable of

maintaining. They also affect anion resin performance and can cause fouling.

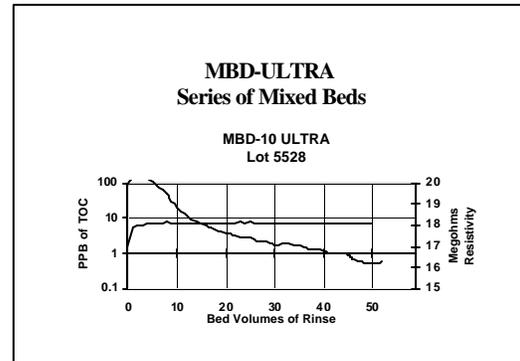
Leachables from anion resins are significantly different than the leachables from cation resins. Anion leachables are predominately caused by amine instability. The dominant leachable from Type I resins is trimethylamine, which can be removed by cation exchange resin. However, there are secondary oxidation routes that create non-ionized leachables such as methanol that will escape from the deionization system and appear as TOC in the effluent. Organic leachables from anion resins are usually low molecular weight materials and unlike cation resins do not usually have an aromatic component.

In today's semiconductor and high pressure boiler applications, the minimization of TOC leachables is extremely important. It is increasingly necessary that both the cation and anion resins be vigorously treated shortly before use to reduce the concentration of organic leachables. Cycling new ion exchange resins many times prior to use is one method of purging organics, but can contribute unacceptable levels of sodium and other inorganic ions to the resins. Some resin suppliers now offer special grades of virgin resins in with extremely low levels of leachable organics, in some cases, the very first cycle produces virtually no organic leachables while still maintaining "virgin" purity levels for inorganic ions.



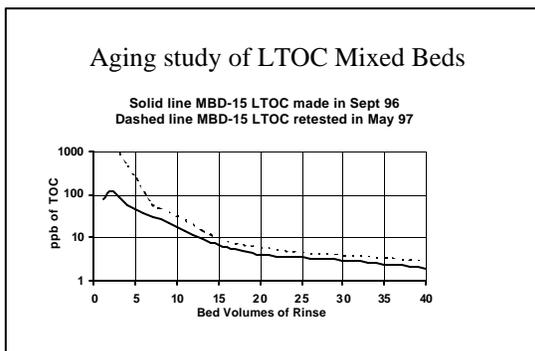
Removal of Leachable TOC from New Resins

It is impossible in the manufacturing process of ion exchange resins, to completely avoid leachable TOC. No matter how careful the polymerization and subsequent functionalization steps, there is always some residual monomer and other contaminants left in the resin. Resins gradually deteriorate as they age and may also contain deep inside the beads, slow to diffuse TOC left over from the manufacturing. The result is a gradual increase of TOC if the resins are left in storage. It is practically impossible for an end-user to purchase and use a resin within hours or days of its manufacture. This means that new resins will always contain some leachable TOC.



Key Points with Respect to Leachables:

1. Type II resins (and for that matter any non Type I resins), when oxidized, produce a relatively high fraction of non-ionized leachables. Their low TOC applications are for the time being, not practical.
2. Acrylic resins are less stable than styrenic resins. They also have lower selectivities for inorganic ions. Acrylic resins for the time being, are not practical in polishing beds used for ultra-pure water applications.
3. The dominant leachables from cation exchange resins are sulfonated aromatic compounds that can kinetically foul the anion exchange resins.
4. Hydrogen form cation resins are slightly unstable and can develop high levels of sulfonated aromatic leachables during storage. For this reason, hydroge form



cation resins should be used relatively soon after manufacture or must be rinsed or cleaned prior to use.

5. Increasing cross-linkage increases oxidative stability (and reduces gel phase diffusion rates) thus decreasing the buildup of TOC leachables over time. This is true both in cation and in anion resins.
6. Whatever cleaning process is used to remove leachables, it must be done in such a way as to not damage the physical characteristics or chemical purity of the resin.