

Apparatus and method for providing ultrapure water

This invention relates to an apparatus and a method for providing ultrapure water, in particular it relates to an apparatus and method for providing ultrapure water for use in semiconductor fabrication.

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Ultrapure water is necessary as a cleaning medium in the production of electronic components for semiconductor chips (logic chips, DRAM (Dynamic Random Access Memory), NAND flash memory, and many more), integrated circuits, microsystems, medical devices, sensors and the like. The already high requirements to the quality of ultrapure water are still increasing in view of the ongoing structural miniaturization towards nanometer scale of these electronic components. Therefore, e.g. the particle content, the metallic impurities, ion content as well as the TOC (Total Organic Carbon) content has to be as low as possible (from sub ppb (parts per billion) level for TOC to ppt (parts per trillion) for ions down to ppq (parts per quadrillion) level for metals).

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Normally, the production of ultrapure water takes place in several process steps, grouped into the so called Pre-treatment, the so called Make-Up and the so called Polishing section. The final Polishing-steps treat water pretreated through pre-treatment and Make up section further, in order to meet the requirements of microelectronics and similar technologies.

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As a consequence, any corrosion and metallic particle release into the treated water should be avoided. In this context, it is preferred that the content of metallic particles in ultrapure water is at least less than 0.1 ppt (parts per trillion).

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However, according to the state of the art, vessels used in the Polishing steps for ultrapure water, e.g. in state of the art photolysis reactors (UV/VUV-reactors) are all made from stainless steel, as polymeric materials are not withstanding to UV light (≤ 400 nm) over long term.

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In this context "UV" means "ultraviolet (radiation)". "VUV" means "vacuum ultraviolet (radiation)".

Further, in the prior art normally at least three separate devices are used in the Polishing steps to produce ultrapure water, namely an UV reactor, a device comprising at least one ion exchange resin and a device comprising at least one catalyst immobilized on a support. These devices and their arrangement in a plant take up a lot of space.

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Therefore, on the one hand there is a general market demand in the ultrapure water production, in particular for semiconductor use, to have less and less contact between the water and metals and their alloys (e.g. steel) in the Polishing steps of this ultrapure water production. On the other hand, there is need for an improved apparatus for providing ultrapure water, which overcomes
5 drawbacks of the presently known apparatus. In particular, there is a need to find an apparatus which reduces the high space requirement of apparatuses known from the prior art.

To overcome these drawbacks and to fulfil these needs the invention provides an apparatus for providing ultrapure water, in particular ultrapure water for use in semiconductor fabrication with
10 the features of claim 1. Preferred embodiments of the inventive apparatus are defined in the claims dependent from claim 1.

Further, the invention provides a method for providing ultrapure water with the features of claim 15, and an inventive use of the inventive apparatus with the features of claim 16.

15 The wording of all claims is hereby explicitly incorporated into this description by reference.

According to the invention, an apparatus mentioned above comprises at least one cylindrical reactor with an inner cylindrical shell, an outer cylindrical shell and a channel-like volume
20 between inner shell and outer shell. Said inner cylindrical shell houses at least one UV emission device. Said outer cylindrical shell comprises at least one means for reflecting UV radiation. And said channel-like volume is provided for flowing water through the reactor.

In other words: the inventive apparatus comprises two tubes or pipes which are arranged
25 concentrically. Due to this arrangement a space between the two tubes/pipes is formed which has an annular cross-sectional area. The at least one UV emission device is arranged within the inner tube/pipe. The water flows through the space between inner tube/pipe and outer tube/pipe. The outer tube/pipe comprises the at least one means for reflecting UV radiation.

30 As already explained above, the term "ultrapure water" (UPW) is water that has been purified to very strict specifications. This water should by definition contain only H_2O , and H^+ ions and OH^- ions in equilibrium. As also already mentioned, ultrapure water is mainly used in the semiconductor industry, and also in the pharmaceutical industry, possibly at a lower purity grade.

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According to the invention, the term "UV emission device" shall include any source which is capable to emit electromagnetic radiation with a wavelength between 10 nm and 400 nm. These sources can be so called UV lamps, like short-wave ultraviolet lamps, halogen lamps, gas-discharge lamps, excimer lamps, and can also be ultraviolet LEDs and ultraviolet lasers.

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Preferably, an UV lamp is placed in the inner shell (cylinder) in a gas atmosphere, in particular in an atmosphere of air, nitrogen (N₂) or other inert gases, e.g. noble gases like argon.

10 In preferred embodiments of the inventive apparatus the inner cylindrical shell is made from SiO₂ (quartz), in particular from synthetic crystalline SiO₂. Such quartz materials, in particular quartz glasses have an excellent (maximum) optical transmittance for ultraviolet light. These materials are known as "synthetic UV-grade fused silica". These materials consist of a high-purity synthetically produced molten quartz material.

15 According to the invention it is preferred that the UV emission device has an emission spectrum with wavelength ≤ 380 nm, wherein preferably said emission spectrum includes emission peaks ≤ 200 nm. In this context, it is further preferred if the emission spectrum includes at least emission peaks of 185 nm and of 254 nm.

20 As a preferred example for an UV emission device, a mercury low pressure UV lamp emits 90 % UV light with a wavelength of approximately 254 nm and 10 % UV light with a wavelength of approximately 185 nm. In particular the UV light with wavelength of 185 nm produces OH-radicals in water which can oxidize trace organic impurities to organic acids or even can mineralize those organic impurities to e.g. CO₂/HCO₃⁻-ion, or to SO₄²⁻, Cl⁻-ions, and NO₃⁻-ions.

25 Those resulting substances will be removed completely by ion exchange resins in a further Polishing step for the ultrapure water.

According to the invention it is preferred if the outer cylindrical shell in an inventive apparatus is (also) made from SiO₂ (quartz). As the UV light from the UV emission device has already

30 passed the water to be treated in the channel-like volume, use of a quartz material with a lower UV transmission rate (compared to ultrapure synthetic crystalline SiO₂) is sufficient as a material for the outer cylindrical shell.

Referring to the means for reflecting UV radiation in the inventive apparatus, use of different

35 means is possible. E.g. use of a shield, in particular a foil surrounding the outer cylindrical shell at its outer surface is possible. Such shields can be made from an UV reflective metal, in particular from aluminum.

Nevertheless, according to the invention it is preferred if said means for reflecting UV radiation is at least one coating, which can be provided also in particular at the outer surface of said outer cylindrical shell. Also the coating can be made from any UV reflecting material, e.g. a metal like aluminum. Nevertheless, it is preferred if such a coating is made from SiO₂, preferably from amorphous SiO₂.

In principle the dimensions of the channel-like volume in the inventive apparatus are not critical. However, in order to support an effective treatment of the water with UV light it is preferred that the channel-like volume has a width between 0.1 mm and 100 mm. In particular said width is between 2 mm and 50 mm, preferably between 2 mm and 15 mm.

According to the invention, one continuous channel-like volume can be provided between inner cylindrical shell and outer cylindrical shell. In these cases, the water to be treated flows between the two shells along the channel-like volume unhindered. However, it is also possible and preferred according to the invention that said channel-like volume is made up from at least two chamber-like sections which are arranged (along the shells) in series. With these embodiments the water is treated with UV light in each section separately. These embodiments can also be used with advantage if more than one UV emission device is provided in the inner cylindrical shell. In these cases one UV emission device can be provided for each section of the channel-like volume so that the water is treated in each section by the UV light of another emission device one after the other.

With further preferred embodiments of the inventive apparatus the channel-like volume comprises means for generating a turbulent flow of flowing water in said volume. With this measure, contact between UV light and water and contact of the components in the water will be intensified and the efficiency of the UV treatment increases. For example, there will be an improved homogeneous distribution of OH radicals in the water for their reaction with organic impurities. Those OH radicals are primarily formed near to the UV emission device in the water close to the inner shell and are better distributed in the water volume by said means.

Said means for generating a turbulent flow are preferably static means which are firmly installed in the channel-like volume. In particular said means are spiral components, preferably spiral components made from SiO₂. In this context, use of spiral components made from crystalline SiO₂ as mentioned before is preferred, because of their high UV transmission rate, their chemical stability and stability against UV light

Further, in preferred embodiments the inventive apparatus comprises a cylindrical shield enclosing that outer cylindrical shell of the cylindrical reactor. This additional cylindrical shield formed also like a tube or pipe houses and protects the cylindrical reactor, preferably with only slightly larger dimensions. This additional shield also defines a boundary surface to further
5 components included in a device for providing ultrapure water.

Said additional cylindrical shield is preferably made from plastic or has at least a surface made from plastic.

10 According to the invention, in principle the overall dimensions of the inventive apparatus are not critical. However, it is preferred, if the inventive apparatus (reactor), including a cylindrical shield (where applicable) has a length/height between 500 mm and 3000 mm, in particular between 1000 mm and 2000 mm, and a diameter between 100 mm and 500 mm, preferably between 200 mm and 400 mm.

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In other preferred embodiments of the invention the cylindrical reactor is contained in a vessel, in particular a cylindrical vessel. This vessel can be made from steel, stainless steel or other metallic materials, like titanium and titanium alloys. However, preferably this vessel is (also) made from plastic materials or at least has a surface made from plastic materials.

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According to the invention it is preferred, if said vessel is a pressure vessel which can be used with pressures up to 15 bar.

The vessel, preferably cylindrical vessel can include more than one cylindrical reactor according
25 to the invention, in particular a number of reactors arranged as an array. With this measure, a greater amount of water can be treated with the inventive apparatus. Normally and preferably the cylindrical reactors are installed in the vessel in a way that the water to be treated enters the cylindrical reactor at its bottom and exits the cylindrical reactor at its top.

30 According to further preferred embodiments of the inventive apparatus at least part of the volume between the vessel (containing the cylindrical reactor) and the outer cylindrical shell or at least part of the volume between the vessel and the shield enclosing the outer cylindrical shell is provided for at least one further treating step of that water flowing through the reactor. With this measure a space-saving design of the overall apparatus is possible.

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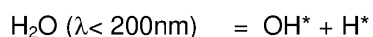
With the last-mentioned embodiments it is preferred that said volume (for further treating the water) is filled at least partly with at least one absorbing material, preferably at least one ion

exchange resin. Further, with the last-mentioned embodiments it is also preferred that said volume (for further treating the water) is filled at least partly with at least one catalyst, wherein preferably said catalyst is immobilized on a support.

- 5 The (outer) volume (for further treating of water) in the last-mentioned embodiments is passed by the water which exits the cylindrical reactor preferably from the top and collected at the bottom of the vessel through nozzles. Then the fully treated ultrapure water of the Polishing steps exits the vessel.
- 10 The catalyst is normally immobilized on an alkaline support (i.e. a anion exchange resin in OH form). The catalyst can be preferably chosen from noble metals, in particular palladium or platinum, in element form with a high surface area. The concentration of the metal will be e.g. 1 g per liter resin. The resin including the catalyst can be layered on top of the mixed bed resin. It can be also layered on mixed bed (ion exchange) resin as a mixture of 5 % to 15 % catalyst
- 15 mixed up with anion resin or mixed bed resin in terms of 50 % to 95 % content, preferably between 10 % and 30 % of catalyst resin.

Preferably, if the filling material is composed of a noble metal catalyst (in particular Pd⁰ or Pt⁰) on an anion exchange resin support, possibly mixed or layered with mixed bed resins, H₂O₂ (hydrogen peroxide) produced in the cylindrical reactor (normally 1 to 100 ppb (parts per billion))

- 20 is removed by a catalytic reaction to produce water (H₂O) and oxygen (O₂). By adding some hydrogen gas (H₂) into the feed water stream of the overall apparatus, the dissolved oxygen (as produced from H₂O₂ above) can be removed by catalytic reaction to produce water. The photolysis reaction producing OH radicals is also producing some H radicals following the
- 25 chemical equation:



Through radical recombination there is generation of more stable H₂O₂ from 2 OH radicals and some H₂ gas from 2 H radicals.

- 30 The produced H₂ gas is participating on the noble metal catalyst (Pd⁰ and/or Pt⁰) to reduce H₂O₂ to H₂O + O₂ and O₂ to H₂O.

As a result an ultrapure water with a residual level of < 10 ppb, resp. < 1 ppb H₂O₂ can be provided at the outlet of the overall inventive apparatus.

- 35 In addition to the inventive apparatus as described above, the invention also includes a method for providing ultrapure water, in particular ultrapure water for use in semiconductor fabrication.

In this method water is flown through a channel-like volume provided between an inner cylindrical shell and an outer cylindrical shell of a cylindrical reactor in an inventive apparatus.

5 Finally, the invention includes use of the inventive apparatus in the production of ultrapure water, in particular in the production of ultrapure water for use in semiconductor fabrication. With this use contact of said ultrapure water with metals or alloys is minimized or even avoided. Preferably this use takes place in the Polishing steps of the production of ultrapure water.

The invention is associated with a number of advantages.

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First, it has to be mentioned that with the inventive apparatus comprising at least one cylindrical reactor with the described features contact of the water with metals or metal alloys can be minimized or even avoided. With the invention the inner cylindrical shell, the outer cylindrical shell and the channel-like volume between the two shells are made from materials, in particular
15 quartz materials, which do not contain any metal. This is also true for any material used in further treating steps of said water, after UV irradiation.

Further, UV irradiation according to the invention is more effective. Normally, UV light with a wave length of 185 nm is absorbed by water after approximately 10 mm to 11 mm. UV light with
20 a wave length of 254 nm can pass water completely. As a consequence, the reflecting means for UV radiation on the outer cylindrical shell have two effects. First, UV light with a wave length of 254 nm is reflected back to the water so that the positive concentration of OH radicals can be increased by dissociating again H_2O_2 (formed by recombination of OH radicals) to OH radicals. Second, by reflecting the UV light any damage caused by UV radiation outside the cylindrical
25 reactor can be minimized or avoided.

Finally, the invention combines the removal of organic impurities (TOC), the removal of H_2O_2 and the removal of (metal) ions in ultrapure water by UV/VUV-photolysis, catalytic peroxide treatment and mixed bed ion exchange resin in one sole device instead of three individual
30 devices without any contact of water with metallic, in particular steel parts.

Further advantages and features of the overall invention will be become clear from the following description of the drawings and the example in conjunction with the dependent claims. The individual features can be realized either singly or jointly in combination in one embodiment of
35 the invention. The drawings and the example only serve for illustration and better understanding of the invention and are not to be understood as in any way limiting the invention.

In the drawings show

- Fig. 1 a schematic sectional view of an apparatus according to the invention,
- 5 Fig. 2A and 2B schematic sectional views of essential parts of the inventive apparatus according to Fig. 1,
- Fig. 3 further schematic detail views of the inventive apparatus according to Fig. 1,
- 10 Fig. 4 schematic detail views of another apparatus according to the invention with spiral components, and
- Fig. 5 a schematic isometric view of an apparatus according to the invention with spiral components.
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Apparatus 1 according to Fig. 1 comprises one elongated cylindrical reactor 2 of tubular shape. This cylindrical reactor 2 has an inner shell 3, an outer shell 4 and a channel 5 (channel-like volume) between inner shell 3 and outer shell 4. In other words: cylindrical shell 3 is arranged

20 concentrically in cylindrical outer shell 4.

As also shown in Fig. 1 inner cylindrical shell 3 houses a UV emission device 6, e.g. a mercury low pressure UV lamp.

25 On the outer surface of the outer cylindrical shell 4 there is a coating 7 as a reflecting means for UV radiation. This is not shown in Fig. 1 in detail, but the corresponding coating is explicitly shown in Fig. 2A and 2B.

The water treated in the inventive apparatus 1 flows through channel 5 from the bottom to the top of apparatus 1. This is illustrated by the left arrow at the very bottom of Fig. 1.

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Fig. 1 further shows

- support rod 8 which increases mechanical stability of cylindrical reactor 2 between inner shell 3 and outer shell 4,
- 35 - cable 9 for power supply of UV emission device 6,
- elongated cylindrical shield 10 enclosing outer shell 4,

- cylindrical vessel 11 housing cylindrical reactor 2, and defining a volume 12 between shield 10 and vessel 11, and
- absorbing material 13, e.g. ion exchange resins and/or catalysts immobilized on a support for further treating steps of the water flowing through the reactor.

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According to preferred embodiments of the invention, in the apparatus 1 of Fig. 1 inner shell 3 is made from synthetic ultrapure crystalline quartz and outer shell 4 is made from crystalline standard quartz. The UV reflective coating 7 on the outer surface of shell 4 is also made from amorphous Silica.

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Fig. 2A includes a larger view from the top part of apparatus 1 (see Fig. 1), and Fig. 2B includes a larger view of the bottom part of apparatus 1 (see Fig. 1).

Also, according to Fig. 2A cylindrical reactor 2 comprises inner cylindrical shell 3 (housing UV emission device 6), outer cylindrical shell 4 (comprising an UV reflecting coating 7 at its outer surface), and channel 5 between inner shell 3 and outer shell 4.

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Further, Fig. 2A shows power supply cable 9 for UV emission device 6. Also illustrated are cylindrical shield 10 and vessel 11, defining volume 12 between them.

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By the arrows in Fig. 2A it is also shown that the water treated in apparatus 1 flows in channel 5 from the bottom to the top, and is then redirected to flow from the top to the bottom through volume 12.

Also, in Fig. 2B the same components of apparatus 1 are illustrated as in Fig. 2A. Therefore, cylindrical reactor 2 comprises inner cylindrical shell 3, outer cylindrical shell 4 and channel 5 (channel-like volume) between inner shell 3 and outer shell 4. UV emission device/lamp 6 is arranged within inner shell 3. Coating 7 is provided at the outer surface of outer shell 4 as an UV reflective means. Further, support rod 8 between inner shell 3 and outer shell 4 is shown in Fig. 2B.

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Outer shell 4 is shielded by cylinder 10. Vessel 11 houses cylindrical reactor 2 with volume 12 between cylindrical shield 10 and vessel 11.

The water to be further purified in apparatus 1 flows into the apparatus from the bottom (see "inlet"), and then flows through channel 5 to the top of apparatus 1 (see illustration in Fig. 2A).

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Redirected water flow is channeled through volume 12 for further treatment, and exits apparatus 1 at its bottom (see "outlet" in Fig. 2B).

Fig. 3 shows two other detail views of apparatus 1 (see Fig. 1), namely the bottom part of
5 cylindrical reactor 2 in apparatus 1.

In this context, on the left Fig. 3 illustrates in a sectional view inner cylindrical shell 3 and outer
cylindrical shell 4 with support rod 8 between inner shell 3 and outer shell 4. Further, inner shell
3 and outer shell 4 define channel-like volume/channel 5 between them. The water to be treated
10 will flow into cylindrical reactor 2 from the bottom and then into channel 5 up to the top of
cylindrical reactor 2 (not shown in Fig. 3).

The detail view on the right side of Fig. 3 is a sectional view of the left illustration of Fig. 3 at the
position of support rod 8. Besides inner shell 3, outer shell 4 and channel 5, this sectional view
15 also shows that there are three support rods 8 at a radial distance of 120°.

UV reflective coating 7, which is illustrated at the outer surface of outer shell 4 in the left
illustration of Fig. 3 is not shown in the right illustration of Fig. 3.

20 Fig. 4 shows detail views of another cylindrical reactor 2 in an inventive apparatus, which differs
from the cylindrical reactor 2 shown in Figs. 1 to 3 by the presence of a static means for
generating a turbulent flow in the form of spiral components.

In this context, Fig. 4 in its left illustration shows cylindrical reactor 2, inner cylindrical shell 3,
25 outer cylindrical shell 4 and channel 5 between these two shells 3, 4. Further, this illustration
also shows an UV reflective coating 7 on the outer surface of outer shell 4.

According to the left illustration of Fig. 4, in this embodiment of the cylindrical reactor 2 spiral
components 14 are provided within channel 5. This/These spiral component(s) 14 wind(s) up,
30 preferably in a number of consecutive spiral segments, from the bottom of the cylindrical reactor
up to the top of the cylindrical reactor.

As explained earlier spiral component(s) 14 has/have the function of a static mixer and
turbulence promoter to get better homogeneity of the OH radicals produced by UV light in their
35 interaction with the organic molecules which have to be oxidized.

In the other illustration of Fig. 4 on its right side, a sectional view at the position of the turning point of component 14 (left illustration in Fig. 1) is shown. This sectional view shows inner shell 3, outer shell 4, and spiral component 14 within channel 5.

- 5 For an even better understanding of an apparatus and cylindrical reactor including spiral components Fig. 5 shows such a cylindrical reactor 2 in an isometric view. This isometric view illustrates inner cylindrical shell 3, outer cylindrical shell 4, and channel 5 between these two shells 3, 4. Further, Fig. 5 illustrates spiral component(s) 14 winding up in the channel 5 in the form of segments.

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EXAMPLE

An apparatus/device as shown in Fig. 1 with reference sign 1 has a height/length of 1700 mm and a diameter of 300 mm of its cross sectional area. This apparatus comprises a cylindrical reactor (reference sign 2 in Fig. 1) with a length of 1500 mm. The inner cylindrical shell (reference sign 3 in Fig. 1) of the cylindrical reactor houses a mercury low pressure lamp with an electric power of 300 W. The width of the channel-like volume (reference sign 5 in Fig. 1) in the cylindrical reactor is 11 mm.

- 20 Further, the apparatus used in the example comprises a catalyst resin and an ion exchange resin (in the volume designated with reference sign 12 in Fig. 1) for further treating the water after the UV-treatment step. In the example, the apparatus contains 25 liter of catalyst resin (strong base anion exchange resin with 1 g/L Pd⁰) and 50 liter of mixed bed ion exchange resin (UPW grade).

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With the described apparatus two feedwater samples (pretreated through pre-treatment and MakeUp section) are further treated to provide ultrapure water. These (pretreated) ultrapure water samples include ethanol as an organic molecule to be oxidized.

- 30 1. The first feedwater sample comprises 9.3 ppb TOC and is treated in the apparatus with a capacity of 1 m³/h at a temperature of 22 °C.

After treatment with UV-radiation in the inventive cylindrical reactor the ultrapure water contains 6 ppb TOC and 41 ppm H₂O₂. After further treatment by the catalyst resin and the mixed bed ion exchange resin, i. e. after the final polishing step, the ultrapure water has 0.9 ppb TOC and 3 ppb H₂O₂.

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2. The second feedwater sample comprises 30.3 ppb TOC and is treated in the apparatus with a capacity of 2 m³/h at a temperature of 22 °C.

5 After treatment with UV-radiation in the inventive cylindrical reactor the ultrapure water contains 23.1 ppb TOC and 62.8 ppm H₂O₂. After further treatment by the catalyst resin and the mixed bed ion exchange resin, i. e. after the final polishing step, the ultrapure water has 2.9 ppb TOC and 3.6 ppb H₂O₂.
