

Device for measuring the purity of ultrapure water

[Detailed description of the Invention]

5 [Technical field]

The present invention relates to a device for
executing a method for analyzing the level of purity of a
liquid obtained after purification treatment and in
particular the level of purity of so-called ultrapure
10 water (less than 10 parts per billion (ppb)).

[Background art]

The method generally employed for purifying water
or any other liquid begins with passage through a first
15 device comprising filtration and purification means such
as activated carbon filtering, ion exchange resin
filtering or reverse osmosis filtering. At the outlet of
the first treatment means, the ultrapure water contains
very few ions and is characterized by a resistivity close
20 to or equal to 18.2 MΩ.cm, but still contains organic
compounds. The ultrapure water is then passed through a
second device in which the organic compounds are oxidized
in order to ionize them. During the oxidation, the
organic compounds are degraded and at this time, the
25 carbon atoms are present in the form of carbon dioxide
gas, which is dissolved in water to form bicarbonate ions
HCO₃⁻. This oxidation is obtained by passage in front of
an ultraviolet lamp or by adding hydrogen peroxide.

The third purification step consists of refining
30 the water, i.e. passing it through an ion exchange resin
that blocks the ions created during the preceding step
and thus completes the purification of the water. During
this step, the organic compounds that were not degraded
during the oxidation phase are not affected.

35 The purity of the water obtained at the end of this
process remains undetermined. One method commonly
employed measures the resistivity of water at the outlet

from the oxidation means, which is directly linked to the dissolved carbon dioxide gas content, i.e. to the number of bicarbonate ions, and then the resistivity of water is determined if the oxidation process had been continued until the end, i.e. if all of its organic compounds had been degraded. This process requires an infinite time period and can obviously not be used. Therefore, it is necessary to employ methods of estimating the limit resistivity.

10 A device and a method for analyzing the purity of water that utilize the difference in the resistivity of the water between the upstream and downstream sides of the oxidation means to estimate this resistivity at infinity is already known, in particular from the patent
15 EP0581157 by Millipore Corporation. This method uses the device in a first or reference mode to measure the resistivity difference between the upstream side and the downstream side of the oxidation means on water samples that have been exposed to the oxidation means for various
20 duration of times. The exposure times are typically of the order of 10, 20, 30, 40, 50 and 60 seconds. By extrapolation from the curve obtained, it is possible to determine what the resistivity of the water obtained would be after an infinite exposure time, i.e. if all the
25 carbon atoms were degraded. Using an appropriate modeling program, such as the MINTEQA2 program described in the publication EPA/600/3-91/021 (1991) of the US Environmental Protection Agency, it is possible to determine the total organic carbon (TOC) content in the
30 reference water from the resistivity at infinity.

 To determine its content of organic compound impurities and thus to verify that purity of water remains nominal, a second or purification or analysis mode in which ultrapure water is passed at a given
35 flowrate through oxidation means is used thereafter. The resistivity difference between the upstream and downstream sides of the oxidation means is measured

continuously and the total amount of organic compounds is deduced therefrom by means of an assumed linear relationship between the resistivity difference measured in the purification mode and the resistivity difference at infinity estimated in the reference mode.

[Summary of the Invention]

[Problems to be solved by the invention]

10 An object of the present invention is to propose a device for analyzing the amount of organic compounds existing in a liquid at the outlet from a purifier that is more economical and easier to use.

15 [Means for solving the problems]

 To achieve the above-mentioned object, the present invention provide a device for analyzing an amount of organic compound in liquid such as ultrapure water at an outlet of a purifier comprising a filter means 1, an oxidation means 2, and a purification means 3 in series and further comprising a means for measuring resistivity of water 4 to determine the purity of water, characterized in that the means for measuring comprises only one resistivity measuring cell 4;

25 a connection means and a fluid circulation control means are configured so as to:

 - prohibit circulation of fluid between an outlet point 12 of the filter means 1 and an inlet point 21 of the oxidation means 2 and to allow circulation of fluid between the outlet point 12 of the filter means 1 and an inlet point 41 of the resistivity measuring cell 4, or

 - to allow circulation of fluid between the outlet point 12 of the filter means 1 and the inlet point 21 of the oxidation means 2 and to prohibit circulation of fluid between the outlet point 12 of the filter means 1 and the inlet point 41 of the resistivity measuring cell 4.

The reduction to a single cell avoids encountering uncertainty, in particular when the calculation uses the value of the difference between a number of cells, and most importantly reduces costs since, given their
5 complexity, these cells account for a large part of the overall cost of the device.

According to preferred features intended to simplify the production of the liquid circuit,

- said resistivity measuring cell is arranged
10 between the outlet point of the oxidation means and the inlet point of the purification means in series in the circuit;

- the outlet point of the filter means is connected to said resistivity cell by a branch circuit comprising a
15 check valve that is open only if the pressure at the inlet reaches a predefined value;

- the outlet point of the filter means is connected to the inlet point of the oxidation means by a simple analysis valve with two positions, open and closed;

20 - the two-position valve is arranged on the downstream side of the starting point of the branch circuit;

- the analysis valve and the measuring means are connected to a control and calculation unit including a
25 control module arranged to command opening and closing of the analysis valve in a predefined sequence and a calculation module arranged to collect the resistivity value from said measuring cell to deduce the purity of the water therefrom in real time.

30 The disclosure of the invention continues next with the description of a preferred embodiment below by way of nonlimiting illustration and with reference to the drawings.

[Brief description of the drawings]

35 - figure 1 is a diagram of a prior art water purifier.

- figure 2 is a diagram of a water purifier of an

embodiment of the present invention.

5 - figure 3 is a curve representing the decrease of the resistivity of the water from any value, in the reference mode, according to the time spent in the reactor, using a prior art approximation method.

10 - figure 4 is a curve representing the decrease of the resistivity of the water from any value, in the reference mode, according to the time spent in the reactor, using the approximation method for the present invention.

Embodiments

15 Figure 1 shows a prior art water purifier comprising, in series, a filter means 1, an oxidation means 2 and a water purification means 3. Two cells for measuring the resistivity of the water 4 are inserted into the circuit respectively at the outlet of the filter means 1 and at the outlet of the oxidation means 2.

20 The filter means 1 typically consist of filters based on activated carbon such as those marketed by Millipore Corporation under the trade mark Q-GARD®. At the outlet of these filter means, the water has a purity of approximately 10 ppb and a resistivity close to or equal to 18.2 MΩ.cm.

25 Here, the oxidation means 2 consist of a mercury vapor UV lamp radiating in the range from 185 to 254 nanometers. The water that flows through the purifier is exposed to this radiation for time periods from 2 to 120 seconds.

30 The purification means 3 typically consist of an ion exchange resin and produce water with a final purity of the order of 1 to 5 ppb.

35 Water enters the device through the inlet point 11 of the filter means. The outlet point 12 of the filter means is connected by a pipe to the inlet point 41 of the first resistivity cell 4 to which the outlet is connected to a three-way valve 16. This three-way valve 16 is

connected on the one hand to the inlet point 21 of the oxidation means and on the other hand to an evacuation circuit (not shown). The three-way valve makes the water leaving the filter means to enter the oxidation means 2 or evacuates it from the circuit.

The outlet point of the oxidation means 22 is connected by a pipe to the inlet point 41 of the second resistivity cell 4 to which the outlet point 42 is itself connected to the inlet point 31 of the purification means. The ultrapure water obtained can be used at the outlet point 32 of the purification means.

Figure 2 shows a water purifier in an embodiment of the present invention, comprising in series as described above, the filter means 1, the oxidation means 2 and the water polishing means 3. This circuit differs from the prior art circuit in that it includes only one measuring cell 4 which is arranged between the outlet point 22 of the oxidation means 2 and the inlet point 31 of the polishing means 3 in series, and in that the three-way valve 16 is replaced by a simple analysis valve 6 with two positions, open and closed, that is less costly and easier to use.

Water at the outlet of the filter means is divided between two pipes, one of which goes to the analysis valve 6, as mentioned above, and a second of which, forming a bypass circuit, goes directly to the resistivity measuring cell 4 via a check valve 5 calibrated to open above a certain value.

Water from the filter means 1 is directed either to the oxidation means 2 or directly to the measuring cell 4 via the branch circuit equipped with the check valve 5 entirely by the operation on the analysis valve 6. When the analysis valve 6 is in the open position, it allows liquid to pass to the oxidation means; the pressure in the branch circuit falls and the check valve 5 remains closed. If the analysis valve 6 is closed, the pressure rises in the branch circuit, the check valve 5 opens, and

water is allowed to flow into the resistivity measuring cell 4.

Figure 2 also shows control means for the water purifier comprising a control and calculation unit 7 and a display device 8 configured to provide the operator in real time with information on the purity level obtained. The control and calculation unit 7 controls the position of the analysis valve 6 using a control module 9 and processes information supplied by the resistivity measuring cell 4 in a calculation module 10. The calculation module 10 executes the water purity calculation method and transmits the result obtained to the display device 8.

As in the prior art, the method for measuring the purity of water comprises a first measurement of the resistivity of the water at the outlet of the filter means followed by the use of two separate operating modes of the purifier, that is, a reference mode and an analysis mode. To evaluate the resistivity of the water supplied by the filter means 1, the analysis valve 6 is closed and the pressure on the upstream side of the check valve increases; the valve opens when the pressure reaches the nominal opening value and the flow of liquid circulates in the branch circuit via the check valve 5. In analysis mode or in reference mode, when the analysis valve is open, the check valve 5 prevents circulation of the liquid in the branch circuit, and the pressure at its inlet remains below the nominal opening pressure. The analysis valve is continuously open in analysis mode. However, in reference mode, it remains closed during predetermined time periods in which the water inside of the oxidation means continues to be exposed to the UV radiation. The analysis valve is then opened to send irradiated water to the measuring cell 4. Because of the significantly different time periods, the reference module determines the variation of the resistivity of the water according to the time water situated in the

oxidation means.

The configuration comprising a check valve 5 and an analysis valve 6 means that a single measuring cell 4 can be employed to measure the resistivity at the outlet of the filter means 1 and at the outlet of the oxidation means 2. This is reflected firstly in a significant saving in the cost of producing the device and secondly by greater ease of use, and the three-way valves of the prior art is too complicated to use under the hydraulic operating conditions of the device.

Figure 3 shows a number of points indicating the resistivity of the water at the outlet of the oxidation means 2 according to the time that water situated in the oxidation means. Figure 3 also gives a curve approximating those points by an exponential function of the type $\rho(t) = \rho_{\infty} + (\rho_0 - \rho_{\infty}) e^{-t/T}$. Figure 4 gives the resistivity value of the same points and an approximation curve produced by a mixed (exponential and linear) function, which can be represented as follows:

$$\rho(t) = \rho_{\infty} + (\rho_0 - \rho_{\infty}) e^{-t/T} + \rho_{\text{slope}} t + \rho_{\text{intercept}} \cdot u_{\text{start, length}}(t)$$

where ρ_{slope} and $\rho_{\text{intercept}}$ are the slope and the ordinate at the origin of a linear function and $u_{\text{start, length}}(t)$ is a function having the value 0 on a first portion of the abscissa axis corresponding to a purely exponential function and a value of 1 for the remainder of the abscissa axis where the function can be treated as the sum of an exponential function and a linear function.

The curve of figure 4 is a better approximation of the evolution of the resistivity as a function of the UV irradiation time, especially if the UV reactor has plastic material parts that are in contact with the water and are subjected to this radiation. The linear part of the curve takes into account the presence in the water of organic compounds that are generated by the photo-ionization of plastic materials or by dissolving carbon dioxide gas from the atmosphere. This new approximation curve reduces by 50% the adjustment effected using the

least-squares method.

The process leading to measurement of the purity of the water obtained after it passes through the purifier will be described next.

5 The first operation is to measure the resistivity of the water at the outlet of the filter means 1 by closing the analysis valve 6. The water then flows via the branch circuit and the check valve 5 directly into the resistivity measuring cell 4, which gives the value
10 of the resistivity of the water at the outlet of the filter means 1. This value ρ_{UPW} remains a priori constant throughout the purification operation because it depends only on characteristics of the liquid before purification.

15 Next a series of operations in a so-called reference mode begins. The purpose of this mode is to determine the resistivity at infinity $\rho_{\infty REF}$ of water that serve as a reference fluid for the remaining portions of the measurements. The analysis valve 6 is open for a
20 short amount of time, that is, it opens for the time to replace water existing in the oxidation means with new water coming from the filter means, and subsequently the analysis valve 6 is closed. The valve remains closed for a particular first time period and is then opened so that
25 water retained in the oxidation means flows into the resistivity measuring cell 4; the resistivity value of this water is recorded, and then the same operation is started again by varying the time the water is situated in the oxidation means. A series of measurements of
30 resistivity are obtained as above according to time and regression techniques are used to deduce the best approximation curve passing through these points in a diagram which provides the resistivity according to time. Then, resolution of the parameters of the function
35 $\rho(t) = \rho_{\infty REF} + (\rho_0 - \rho_{\infty REF})e^{-t/T} + \rho_{slope} t + \rho_{intercept} \cdot u_{start, length}(t)$, which has been unknown up until this point, i.e. the parameters $\rho_{\infty REF}$, ρ_0 , T , ρ_{slope} , $\rho_{intercept}$ and the cut-off

point of the function $u_{\text{start, length}}$ is obtained. This function with six unknown parameters requires experiment to be carried out with at least six different durations. This solution method determines the parameter $\rho_{\infty\text{REF}}$ which gives the value of the resistivity of water particularly when water remained in the oxidation means for an infinite time, in other words, when all the organic components in water had been degraded into bicarbonate ions.

The knowledge of these two values (values ρ_{UPW} of the resistivity at the outlet of the filter means and value $\rho_{\infty\text{REF}}$ of the resistivity at infinity after complete oxidation) begins the phase of analyzing the water coming from the purifier and of knowing the carbon atoms concentration of water at all time, i.e. the purity level of the water. To achieve the purpose, the analysis valve is continuously left open.

The water that has passed through the filter means flows at a given flow rate through the oxidation means in which the water is subject to partial degradation of the organic compounds and in which the resistivity of water changes due to the dissolution of the carbon dioxide gas generated in this way. At the outlet of the oxidation means, the water resistivity ρ is measured by the measuring cell 4 and it is a function of the residence time t during which the water continues to be exposed to irradiation by the oxidation means 2.

Using the single exponential curve for the resistivity evolution model, it is expressed as $\rho(t) = \rho_{\infty} + (\rho_{\text{UPW}} - \rho_{\infty}) e^{-t/T}$. The approximation, which is applied here and consists in retaining only the exponential part of the curve for the changes in resistivity according to time and which could not have been taken into account in the reference mode with reactors including plastic material parts, satisfies the condition here, because the exposure times of the water in the UV reactor remain short unlike the case of the

reference mode.

The value to be determined next is the value ρ_{∞} that is used to obtain the purity of the water at the outlet from the purifier. This parameter is calculated by an analytical extrapolation method explained below.

To simplify, by designating k_{α} to the ratio between the terms $\rho(t)$ and ρ_{∞} as well as $e^{-\alpha}$ to the formula $e^{-t/T}$, $1/k_{\alpha} = 1 + (\rho_{UPW}/\rho_{\infty} - 1) e^{-\alpha}$ is obtained.

By stating that this formula applies equally to the reference mode, in the left-hand portion of its curve ($u_{start, length}(t) = 0$) for the same residence time, $K_{REF} = \rho(t)_{REF}/\rho_{\infty REF}$, and $e^{-\alpha} = (1 - K_{REF})/K_{REF} \times \rho_{\infty REF}/(\rho_{UPW} - \rho_{\infty REF})$ are obtained.

It is then possible to express k_{α} according to ρ_{∞} and parameters that are known by using the reference mode (K_{REF} , ρ_{UPW} and $\rho_{\infty REF}$).

Using the residence time t as a working parameter intended to tend toward infinity, it is possible to cause k_{α} and ρ_{∞} to change successively until the parameter converges by using a standard iterative method.

The value of the resistivity of the water in the oxidation means is obtained when water remained in the oxidation means for an infinite time, i.e. when oxidation of organic compounds in water continued until completion.

Standard methods, for example, a method used by the MINTEQA2 program work back, at this time, from the value of the resistivity at infinity to the total organic carbon (TOC) content of the water, i.e. purity of the water expressed in ppb.

Multiple variants are possible according to the circumstances, and in this regard, it must be pointed out that the present invention is not limited by such embodiments described and shown above.

CLAIMS

1. A device for analyzing an amount of organic compound existing in a liquid such as ultrapure water at an outlet of a purifier comprising a filter means (1), an oxidation means (2), and a purification means (3) in series and further comprising a means (4) for measuring resistivity of water to determine the purity of water, characterized in that
- the means for measuring comprises only one resistivity measuring cell (4);
- a connection means and a fluid circulation control means are configured so as to:
- prohibit circulation of fluid between an outlet point (12) of the filter means (1) and an inlet point (21) of the oxidation means (2) and to allow circulation of the fluid between the outlet point (12) of the filter means (1) and an inlet point (41) of the resistivity measuring cell (4); or
 - to allow circulation of fluid between the outlet point (12) of the filter means (1) and the inlet point (21) of the oxidation means (2) and to prohibit circulation of fluid between the outlet point (12) of the filter means (1) and the inlet point (41) of the resistivity measuring cell (4).
2. The device according to claim 1, wherein the resistivity measuring cell (4) is arranged in between the outlet point (12) of the oxidation means (2) and the inlet point (31) of the purification means (3) in a circuit in series to analyse the amount of organic compound in the fluid.
3. The device according to claim 1 or 2, wherein the outlet point (12) of the filtration means (1) is connected to the resistivity measuring cell (4) by a branch circuit comprising a check valve (5) which opens only when the pressure of the inlet reaches a predetermined value to analyze the amount of organic

compound in the fluid.

4. The device according to any of claims 1 to 3, wherein the outlet point (12) of the filtration means (1) is connected to the inlet point (21) of the oxidation means (2) by a simple analysis valve (6) with two positions, open and closed.

5. The device according to any of claims 1 to 3, wherein the outlet point (12) of the filtration means (3) is connected to the inlet point (21) of the oxidation means (2) by a simple analysis valve (6) with two positions, open and closed.

6. The device for analyzing the amount of organic compound existing in liquid according to any of claims 1 to 5, wherein the analysis valve (6) and the resistivity measuring means (4) are connected to a control and calculation unit (7) comprising a control module (9) configured to command opening and closing of said analysis valve (6) in a predetermined sequence and a calculation module (10) configured to collect the resistivity value from said resistivity measuring cell (4) to deduce the purity of the water therefrom in real time.