

The relationship between pH and Conductivity in a Lithium Contaminated, De-ionized Water System

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Background

In September 2001, collection lens 22 failed after a service life of about 9.3 million pulses. The only evidence that the lens had failed came from the conductivity cells installed in the collection lens cooling system. The cooling water return conductivity went into alarm and initiated the lens purge system several hours after the lens was de-energized following a period of stacking. High conductivity in the return water is indicative of a septum breach in which water comes into contact with lithium metal which forms lithium hydroxide solution. A slight increase in conductivity was observed at the cell located downstream of the resin column corresponding in time with the return cell that provided a secondary indication of the failure. The pH of the cooling water was checked with pH paper and was expected to be about 8, but a number of measurements that were made showed the pH was 6. The introduction of lithium hydroxide in a de-ionized water system was expected to cause an increase in pH above 7. This disagreement between the expected and measured value of pH provided part of the motivation for work described in this paper.

In general, conductivity cells are not fail-safe devices. The conductivity measurement is based upon the measurement of electric current flow between parallel plates of fixed size and fixed separation distance. The measurement may be affected by contaminant deposition on plate surfaces or by changes in geometry due to plate degradation/erosion or any physical distortion of the plate arrangement.

Three lenses had failed in the summer of 1995 on indication of power supply over-current. The cooling water return conductivity cell in use at the time was reading a high value ($0.8 \mu\text{S}/\text{cm}$)¹ for a number of months preceding the failure of these lenses and did not provide the conductivity alarm or initiate the lens purge system. We speculate that the conductivity cell trip level for the alarm and purge functions was set at a level above that which would indicate failure of the lens septum. With high conductivity water present in the cooling water system, we speculate that the next level of protection would be provided by the power

supply over-current trip. The conductivity cells were replaced in 1995 with those that continue to be in service at this time. The existing cells functioned as intended during the failure of lens 22, but there was some doubt during the initial diagnosis about whether the lens had actually failed. This set of circumstances provided the remainder of the motivation for the work described in this paper.

Purpose

The purpose of this paper is to determine the relationship between pH and conductivity in de-ionized water. Since the conductivity measurement is used to determine the failure of collection lenses, it would be useful to understand the conductivity measurement more thoroughly. In addition, it would be useful to understand whether and when a pH test of the cooling water is indicative of the condition of the collection lens. Finally, it would be useful to develop a method to determine whether or not collection lens cooling system conductivity cells are operating properly.

Test System Description

A conductivity cell test system was assembled as shown in Figure 1. DI water was drawn from a 2 liter bottle by a tubing pump and pumped through a conductivity cell, a resin column, and then returned to the 2 liter bottle. An argon gas purge was established in the two-liter bottle to prevent air from entering the system. The purge would also reduce the partial pressures of other dissolved gases. The HOH resin/oxygen column removes ionic impurities and dissolved oxygen. The resin column/housing used in this test system is the identical model used in the collection lens cooling system.

The conductivity cell used is Leeds & Northrup 4973-001-333-7-000 with a cell constant of 0.01. The conductivity instrument is a Leeds and Northrup 7082 Series Conductivity/Resistivity Analyzer/Controller, the same type used in the collection lens cooling system. The instrument has automatic temperature compensation circuitry. The conductivity instrument output was connected to Accelerator Network Controls System (ACNET) and data was collected through Lumberjack datalogger.

¹ An equivalent unit of the mho is Siemens, abbreviated S. The conductivity unit of $\mu\text{S}/\text{cm}$ is equivalent to $\mu\text{mho}/\text{cm}$ and is used throughout this note.

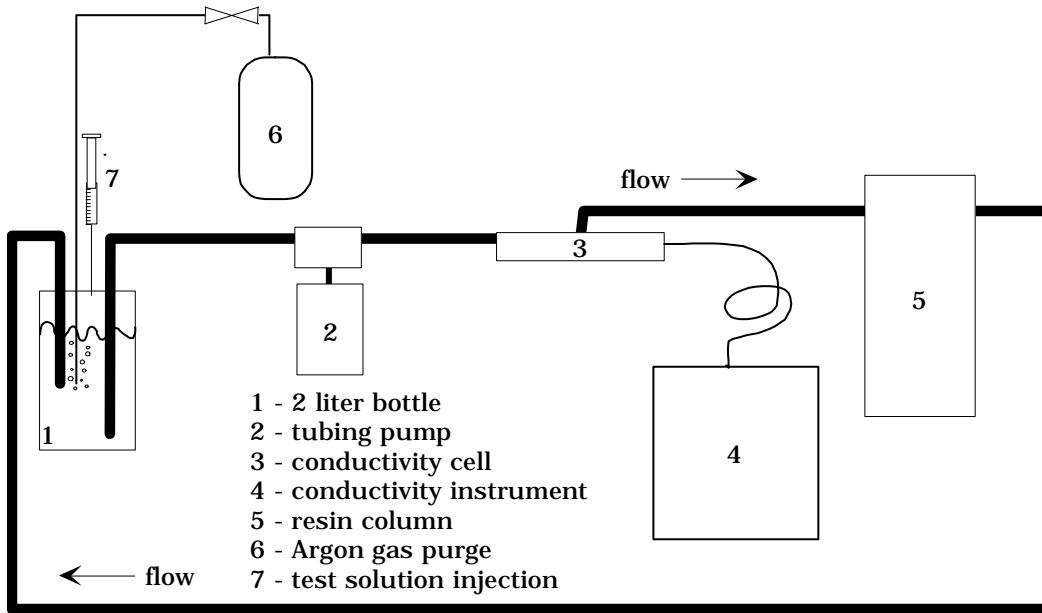


Figure 1

The tubing pump flow is variable with a capacity that ranges from 0 to 1.8 lpm (28 gph) as shown in Figure 2.

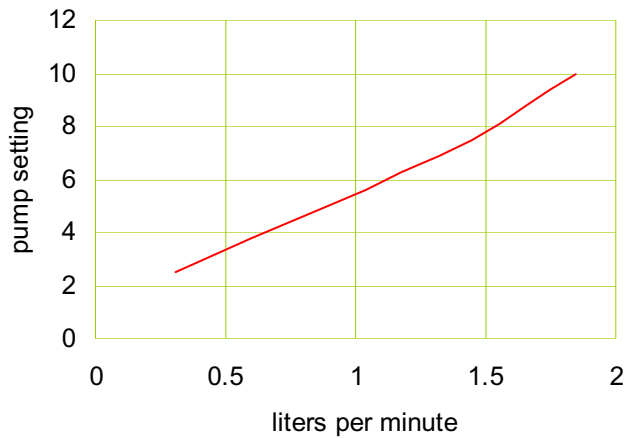


Figure 2 – test system pump flow range

The equilibrium conductivity that can be achieved in this circuit varies with pumping speed. Initial approximate equilibrium conductivity vs. pumping speed is shown in Figure 3. Lower conductivity is

achievable at these pumping speeds after prolonged operation (days). As discussed later in this section, the

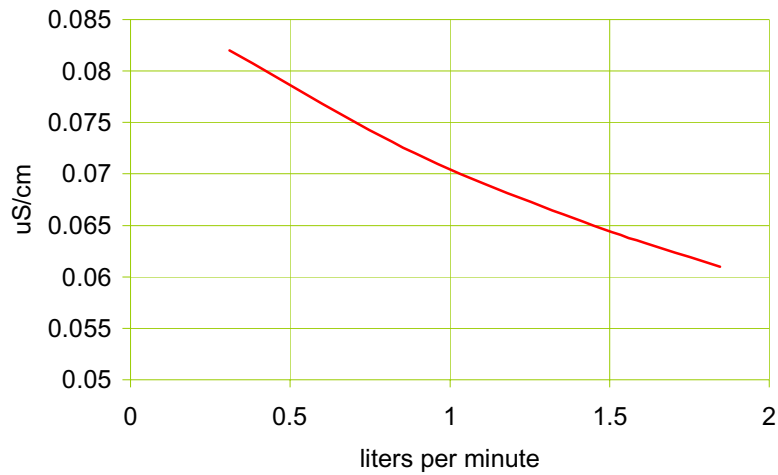


Figure 3 – Test system conductivity vs. flow rate

maximum theoretical conductivity of de-ionized water is about 0.055 uS/cm [3], which may be approachable with this system after prolonged operation. The resin column is rated for about 1.6 lpm (25 gph). The flow rate through the collection lens DI cartridge is typically set at a flow rate of about 3.2 lpm (50 gph). It has been observed that if the flow rate is set at the rated flow, conductivity of the collection lens system climbs to a higher level. Figure 3 provides further evidence of this behavior. There does not appear to be any adverse effect from running at the higher flow. There is some potential for punch through of ions as was noted during the failure of lens 22. The manufacturer’s rated flow value may be the maximum to prevent punch through of ions, but operating experience suggests the column provides lower conductivity levels when operated at flow rates higher than recommended.

The minimum conductivity of de-ionized water can be calculated. The equivalent conductance of an electrolyte is defined as the conductivity of a volume of solution containing one equivalent weight of dissolved substance when placed between two parallel electrodes 1 cm apart, and large enough to contain between them all of the solution [2]. The specific conductance or conductivity in $\mu\text{S}/\text{cm}$ is given by:

$$\text{Conductivity} = \Delta C 1000$$

where C is concentration in mols per liter, Δ is equivalent conductance in $\text{mho}\cdot\text{cm}^2/\text{equivalent}$, and the factor 1000 is necessary for unit conversion. The limiting equivalent ionic conductances of the H^+ and OH^- ions are 349.82 and 198.6 $\text{mho}\cdot\text{cm}^2/\text{equivalent}$, respectively [1]. The product of the molar concentration of hydronium and hydroxal ions in water is constrained by the ionization constant of water:

$$[\text{H}^+] * [\text{OH}^-] = 1 \times 10^{-14}$$

At a pH of 7, $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$. The conductivity of pure water at a pH of 7 is:

$$(349.82 \times 10^{-7} + 198.6 \times 10^{-7}) \times 1000 = 0.0548 \mu\text{S} / \text{cm}$$

A plot of partial conductivity due to H^+ and OH^- ions versus pH water over the pH range 5 to 9 is shown in Figure 4.

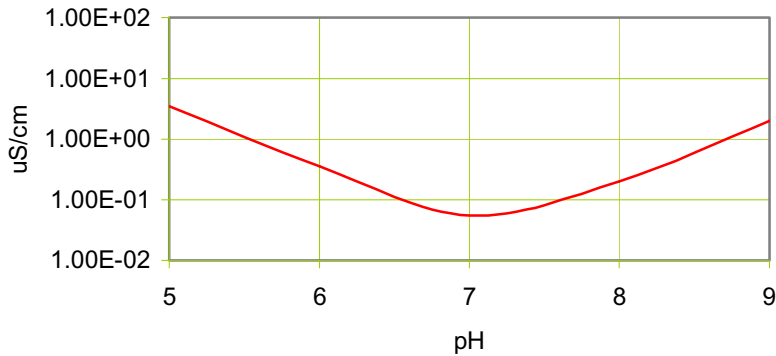


Figure 4 – Partial conductivity vs. pH for pure water

Test System Response Check

A NIST traceable standard solution of known conductivity was obtained to check the conductivity cell response. The standard solution (442 – 15 ppm) contains 6 ppm NaHCO_3 , 6 ppm Na_2SO_4 , and 3 ppm NaCl with a nominal conductivity of 21.3 uS/cm at 20 degrees C.

As an exercise, one may calculate the conductivity of the standard solution using equivalent conductance data from Reference 1 and the manufacturers stated composition as shown in Table 1.

compound	ppm	g/mol	mol/l	Na (mol/mol)	HCO ₃ (mol/mol)	SO ₄ (mol/mol)	Cl (mol/mol)	Na eq. con	HCO ₃ eq. con	SO ₄ eq. con	Cl eq. con	μS/cm
NaHCO ₃	6	84.007	7.14E-5	1	1			50.11	44.5			5.46
Na ₂ SO ₄	6	142.02	4.22E-5	2		1		50.11		80.0		6.68
NaCl	3	58.44	5.13E-5	1			1	50.11			76.35	9.01
											total	21.15

Table 1 – Calculation of standard conductivity from solution components

The calculated conductivity is within 1% of the manufacturers nominal value. Calibration papers are provided with the standard, which gives the actual conductivity of the batch provided with error bars of ± 1%.

In a number of trials, various volumes of this standard solution were injected into the 2-liter bottle while the conductivity response was monitored. The data collection rate was limited to 30-second intervals during these trials and so a slow pump speed was utilized. Figure 5 shows a trial in which 10 cc of the standard solution is injected into 1875 cc of water contained in the 2-liter bottle with the pump flow rate set at 0.3 lpm.

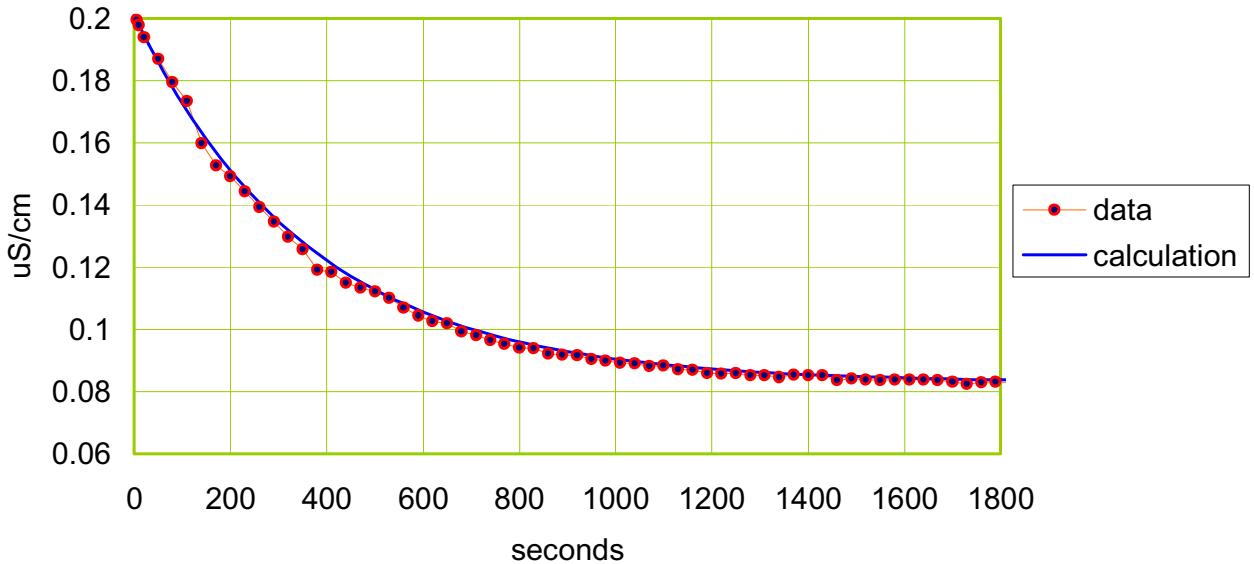


Figure 5 – Measurement and calculation of conductivity vs. time for injection of 10 cc standard

Scaling the standard solution concentration by the dilution factor and adding that value to the base conductivity for a given pumping speed yields the peak conductivity due to injection of the standard solution. Using the parameters for the measurement in Figure 5:

Volume of standard injected	10 cc
Volume of water in bottle	1875 cc
Baseline conductivity	0.083 uS/cm
Conductivity standard	23.8 uS/cm ± 1%

the peak conductivity expected from the addition of the standard is given by:

$$conductivity_{peak} = \frac{volume_{injected}}{volume_{water}} \times conductivity_{standard} + conductivity_{baseline}$$

$$conductivity_{peak} = 0.209 \mu S / cm$$

The measured peak value of 0.201 uS/cm is within 5% of the calculated peak conductivity, a reasonable agreement.

Test System Cleanup Function

The conductivity of the system as a function of time after injection of an impurity, assuming complete removal of the impurity by the ion exchange resin and complete mixing in the water bottle is given by:

$$conductivity(time) = conductivity_{baseline} + \left(conductivity_{peak} - conductivity_{baseline} \right) \times e^{-\frac{lpm}{volume_{bottle}} \times time}$$

This function, plotted in Figure 5 along with the data from the test injection, provides a good prediction of the test system performance.

Calculation of Conductivity Cell Response to LiOH

With an understanding of the conductivity cell response to de-ionized water, a known impurity, and the system cleanup as a function of time, the next point to address is the conductivity cell response for the introduction of lithium hydroxide solution.

The conductivity in $\mu S/cm$ may be calculated by summing the partial conductivity contributions of the stoichiometrically determined ion concentrations, i.e., the removal of H^+ ions in pure water by OH^- ions in the solute must be considered. The equivalent conductance of the Li^+ ion is obtained from Reference 1.

$$conductivity = 1000 \times \left(349.82 \times [H^+] + 198.6 \times [OH^-] + 38.69 \times [Li^+] \right)$$

where:

$$[H^+] = \frac{1 \times 10^{-14}}{\frac{ppm_{LiOH}}{23948.4} + 1 \times 10^{-7}}, \quad [OH^-] = \frac{ppm_{LiOH}}{23948.4} + 1 \times 10^{-7}, \text{ and}$$

$$[Li^+] = \frac{ppm_{LiOH}}{23948.4}$$

The resulting conductivity is plotted as a function concentration in Figure 7 over the range of the conductivity cell instrumentation, i.e., corresponding to 0 to 2 $\mu\text{S}/\text{cm}$.

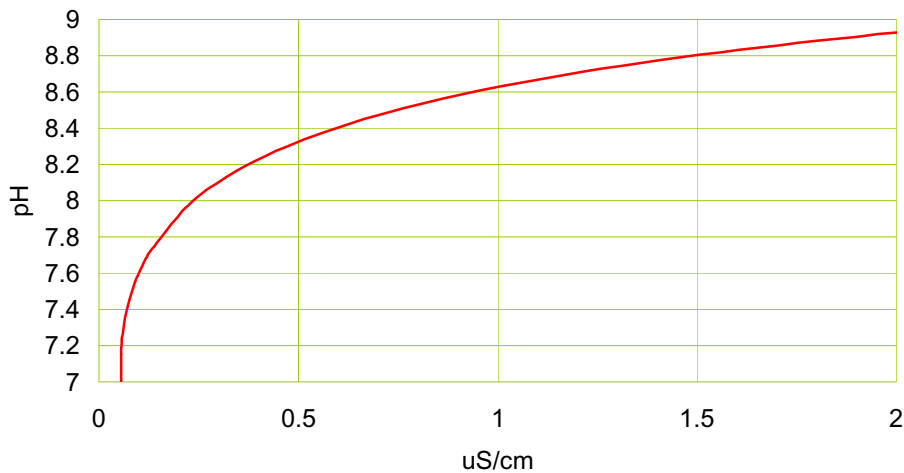


Figure 7 – pH of LiOH in pure water over range of conductivity cell response

Measurement of Conductivity Cell Response to Injection of Unknown LiOH Solution

A LiOH solution of unknown concentration was prepared using reagent grade material previously obtained from Aldrich chemical company. These solutions were tested for pH and were injected into the test system to check the relationship between pH and conductivity. The pumping speed of the system was set at a high flow rate. pH papers used were pHydrion Lo Ion manufactured by Micro Essential Laboratory and colorpHast pH 0-14 manufactured by EM Reagents.

A few grains of LiOH reagent were mixed with 50 cc of DI water. The pH was measured with the 0-14 strips and with the Lo Ion paper with a result 10 and 11, respectively. A series of aliquots of this solution in

volumes of 10, 8, 6, 4, 1, and 0.0176 cc was injected into the 2-liter bottle (1875 cc water) of the test system to check the conductivity response. The result is shown in Figure 8.

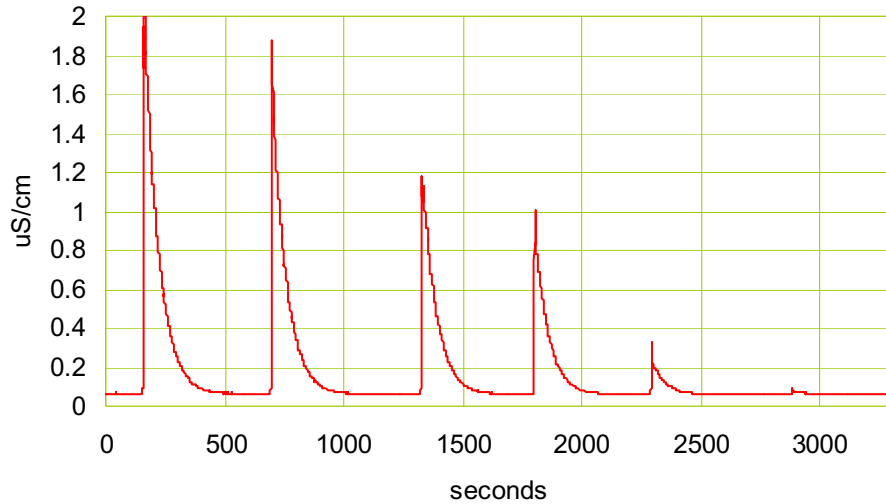


Figure 8 – Series of 6 injections of 10, 8, 6, 4, 1, 0.176 cc LiOH solution

The conductivity response for the 10 cc injection may have gone just off scale. The response for the remaining injections is compared to determine the linearity of the conductivity measurement. The measured conductivity response and the concentration/conductivity relationship derived above are used to determine the concentration of the test solution. In addition, considering system dilution, the initial solution concentration is derived. The results are shown in Table 2. The variation from linear response shown can be attributed to a number of factors including: the relatively high pump speed used in the test, variation in mixing during injections, volume measurement errors, and the datalogger resolution.

Injected Volume (cc)	peak conductivity (uS/cm)	Diluted solution concentration (ppm)	initial LiOH solution concentration (ppm)
10	~2	0.2	37
8	1.88	0.188	44
6	1.13	0.112	35
4	1.006	0.099	47
1	0.316	0.030	57
0.176	0.091	0.006	64

Table 2 Derivation of LiOH solution concentration from conductivity cell response

Based upon the middle 4 injections, the concentration of the unknown LiOH solution is about 46 ppm, which should correspond to a pH of about 11.3. This result agrees well with the Lo Ion pH paper (11), but not so well with the 0-14 pH paper (10).

The pH of the diluted solution was also checked and found to be about 5.5 with both pH papers. As shown in Figure 4, the possibility of obtaining a pH result below 7 in pure water containing lithium hydroxide is excluded. In addition, the pH of the 95 degree LCW system, the collection lens system, and the test system were measured with both types of pH papers and all resulted in a pH of about 5. The conclusion is that these pH papers do not provide reliable indication of pH in low conductivity water. Subsequent checks with pH paper manufacturers substantiate this finding. [4]

Test Methodology for Collection Lens Cooling System Conductivity Cells

A couple of different schemes are possible to check the condition of collection lens cooling system conductivity cells. Simple conductivity cell calibration checks are normally done by dipping the cell in a standard solution and checking the response. This method is not practical for cells used in very pure water systems (cell constant of 0.01) because the conductivity of test solution will generally exceed the upper range of the instrumentation. For this reason, either in-line testing or a system such as that shown in Figure 1 is required.

One method would be to modify the collection lens cooling system piping so that the conductivity cells could be placed in a special test configuration. With the addition of some isolation valves and some additional piping, the cells could be placed in series along with the system's DI column, and a tubing pump and 2 liter bottle similar to the ones used in the test described earlier. A conductivity standard could be injected into the 2 liter bottle and the water would be pumped through the conductivity cells in series. The standard would be removed from the collection lens cooling system by the DI column. The conductivity cells and the related analyzer responses could be recorded by fast time plot and/or by the Lumberjack datalogger. The response of the conductivity cells should be predictable as demonstrated earlier. The disadvantage in this method is that the collection lens cooling system would require some modification. The advantages are that the cell responses could be compared directly to each other and to a known standard, that the system could be tested without disassembly, and that minimal system downtime would be required to perform the calibration.

A second method would be to simply remove the conductivity cells during scheduled maintenance periods, install them in a test circuit similar to the one shown in Figure 1, inject the standard, and monitor the

response. The advantages are that the protocol has been developed as a result of this work. The disadvantage is that the system would have to shut down and partially drained in order to remove the cells.

Conclusions

The conductivity cell response to high purity de-ionized water, a known reference solution, and a series of unknown LiOH solutions has been characterized. The conductivity instrumentation currently in use provides a direct determination of the water quality for the collection lens system. Methods for periodic testing of the collection lens cooling system conductivity cells have been described. pH papers would provide indication of a collection lens failure only in extreme cases. In general, pH papers should not be used in low conductivity water systems. It may be prudent to establish a conductivity test procedure for periodic testing of the collection lens cooling system conductivity cells.

References

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2. Handbook of Chemistry and Physics, 47th edition, 1967, The Chemical Rubber Company
3. OAKTON Tech Tips, <http://www.greenair.com/techtips.htm>
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