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Ultra pure water is used in the manufacturing of semiconductor integrated circuits for both rinsing wafers after numerous cleaning and etching steps and for making up solutions used in these steps. To date, the primary concern has been to produce, deliver and measure the degree of purity of this water. However, as the purity of water goes down, serious problems begin to arise because of the nature of water that does not contain any contaminants. Although the situation is still somewhat theoretical, evidence exists that demonstrates the beginning of such problems. The following paper discusses some problems that already exist and some which will develop during the making, measuring, and using of ultra pure water (UPW).

Specifications for UPW contain limits for resistivity, particles, bacteria, total organics (TOC), silica, anions, cations, metals, and residue (Table 1)¹. Systems designers and facility engineers use these specifications as a means to continuously find ways to meet and to exceed them. As the ability to measure water becomes increasingly more sensitive, the quality of UPW continually becomes purer. The ultimate limit is, of course, water that contains only H₂O in equilibrium with its ions.

Two things must be kept in mind as water reaches its ultimate level of purity. The first is that all materials have some degree of solubility in water, and the second is that

water has a chemistry of its own. Considering the first concern, one first wonders if water can remain pure in processing vessels where it is exposed to the atmosphere and second, what one must do to keep it pure enough for production requirements while wafers are being cleaned, processed, or rinsed in these vessels.

To ascertain whether water at the final filter was any different from the water in processing vessels, a study was conducted on 100 sinks. This work was reported by Theresa Chu in her paper, "Ultrapure Water Testing at the Point of Use"². Basically, she found the following.

TOC levels rose between 20-50 ppb for 50 of the sinks with levels between 50-150 for 40 sinks. Only 10 sinks remained the same. While the incoming water to the sinks was measured at 5-20 ppb TOC, 90 of the sinks never reached the required <20 ppb level which is the specification used for 16 m DRAMS (Table 2)³.

Bacteria, on the other hand, which measured <1-5 colonies per 100 ml at the final filter remained at the same level at 50 sinks while 25 more only increased to between 5-25 colonies per 100 ml. The remaining sinks were between 50-100 colonies per 100 ml.

Bromide, nitrate, nitrite, phosphate, potassium, ammonium, and dissolved silica remained the same in 90 of the sinks tested. However, there was significant evidence that sodium, chloride, and particles did not. Sodium rose from <0.05-.2 at the final filter to as high as 1 ppb in 30 of the sinks tested. Chloride levels rose from 0.05-0.1 ppb to between 0.1->0, 5ppb for 10 of the sinks tested. Zinc, barium, magnesium, and aluminum were also found in some of the sinks in low ppb levels where no metals were detected in the final filter water.

The source of the contaminants found at the POU are no doubt coming from the distribution system, the sinks, and the atmosphere around the sink. However, most tests on distribution loops show insignificant amounts of increase in contaminants. When they are found, they tend to be particles and bacteria.

The increase in TOC, Na^+ , Cl^- , and some metals suggest an environmental problem. Since UPW will dissolve all materials until it reaches the saturation point for that material, any material that comes into contact with it can be absorbed and dissolved. In a fab, regardless of the class rating, organics, chloro-organics, Cl^- (HCl/NaCl), Na^+ (NaCl) and metallic salts and oxides at some levels are ubiquitous. In a recent study done by Balazs Analytical Laboratory using their newly developed air scrubbing sampler, the quantity of NaCl going into a Hepa Filter and immediately coming out of it was measured. Preliminary measurements indicate that as much as 20% of the NaCl that hits a Hepa comes through it. Out of all probability, this NaCl is being carried through in moisture as dissolved salt.

The ability for UPW to absorb and dissolve or react with all kinds of materials complicates other aspects concerning its use in the processing of wafers. These include: (1) getting water through a wet bench where it can leach all the materials that it comes in contact with; (2) putting water into a processing vessel that is dirtier than the water; (3) cleaning any vessel which includes sampling bottles; and, (4) getting UPW samples through analytical equipment without contaminating it before the measurement is made.

This difficulty can be illustrated by taking, for example, the problem that exists when cleaning sampling bottles whether made of glass or plastic. Initially, brand new

bottles contain numerous contaminants both absorbed and adsorbed as atoms (ions), compounds, or particles. Cleaning procedures and solutions must be designed to remove all of the contaminants without adding any of their own. Normally this process is done using acidic or basic solutions and UPW. Bottles that are to be used to test UPW cannot be cleaned using chemicals that are considered ultra pure by the semiconductor industry and that are used in the fab. The concentration of metals in these chemicals is far too high (Table 3 column A). Only those chemicals that have the quality shown in Table 3 column B have metal concentrations low enough that they will not deposit more metals in the containers than the UPW to be tested contains and that will be able to remove any metals that originated in the bottle at levels higher than those in the cleaning solutions. The bottles also need to be soaked in the appropriate solutions several times before they are considered clean. Following this procedure, the bottles need to be thoroughly rinsed with water which also has to be of a higher purity than the water that is to be measured. This requires continuous polishing of the rinse water to the very highest levels of purity attainable. These bottles must then be stored in a way that assures that they remain absolutely clean and free of contamination. If one compares this extensive procedure to that used in a fab site for cleaning vessels, one can realize that these vessels will and do contain contaminants that can be dissolved by UPW. Whether this makes a difference to processing today is questionable, but in the future, especially as water quality improves, it will.

Now if we add to these problems the chemistry of UPW and its reactivity with the walls of the container it is in, further problems are encountered. Such a problem is

evident in some recent work done by Dr. Janos Fucsko at Balazs Analytical Laboratory⁴. Dr. Fucsko is studying the effect of the walls of the tubing on the accurate determination of metals in UPW as they are being measured in an ICP-MS.

Figure 1 is a spectrum showing the ICP-MS measurement of lanthanum (La), bismuth (Bi), and tantalum (Ta) as they come through the instrument over time and in the presence of water, 2% nitric acid, and 1% hydrofluoric acid. The standard solution was made up to be 4 ppb of these elements in UPW. For the first 10 minutes the standard was allowed to flow through the instrument after which the instrument was rinsed with UPW for 10 minutes. Two percent nitric acid was then passed through the instrument until a significant reduction in the concentrations of the metals was seen. One percent hydrofluoric acid was then passed through the instrument.

One can readily see that all three of the metals deposited on the tubing walls were subsequently rinsed out by the stronger acids. Interestingly, La was not completely rinsed out with the nitric acid but rather shows a further reduction in the presence of hydrofluoric acid. Lanthanum fluoride is a very insoluble salt which would be expected to precipitate in hydrofluoric acid. On the other hand Bi and Ta did not rinse out until hydrofluoric acid was used as the solvent. What is of great concern about these results is the fact that the tubing seems to have served as a concentrator for the Ta which shows a maximum concentration in the hydrofluoric acid of 70 ppb.

In figure 2, at the beginning of the hydrofluoric acid rinse, niobium (Nb) shows similar results when a 4 ppb standard is used. However, for Ta, there appears to be no deposition or concentration on the tubing walls which means that the water rinse was

sufficient.

Figure 3 again reveals similar results for rhodium(Rh), iridium (Ir), and indium (In). In this case we again see that the elements do not act the same when they are exposed to UPW, 2% nitric acid and 2% hydrofluoric acid. The Rh is apparently rinsed out completely by the water, the Ir by the nitric acid and the In by the hydrofluoric acid. It is important to recognize that in each case each of the solvents returned essentially to the baseline over time, indicating that the responses for the signal in the ICP-MS was not caused by matrix effects. The more likely explanation is that the organic polymers are acting as ion exchangers which are forming complex solid phase ligands. Wafers can also form such complexes with metals because of the silica that is present.

It is important to emphasize that water cannot clean if it is not cleaner than what it is trying to clean. In the use of water in the semiconductor industry water is generally the cleanest wet agent being used. Consequently, contaminants on a wafer, e.g., acids as well as contaminants in the bath will be drawn into the water and flushed down the drain. However, if a cleaning vessel gets heavily contaminated with metals that have deposited on the walls, the water will absorb them, especially if this water becomes acidic. The water is now the dirtier agent. If the wafer is now the cleanest agent, metals will be deposited onto them. In other words, water can become the transferring agent that carries a contaminant and deposit it onto the wafer. The cleaner the water becomes, the more readily this process will occur.

If temperature is now taken into consideration, new complications are brought into the picture. All materials become more soluble in hot water and it for this reason that

it is being used to rinse wafers. However, hot water becomes a better transferring agent and also will enhance the dissolution of any material that comes into contact with it whether that material is on the cleaning vessel, on the wafer as a contaminant, or a part of the wafer, or in the atmosphere that is in contact with the water. Now we have the issue of the SiO_2 on the wafer going into solution. This phenomenon has already been experienced by those who work with masks. They overcome the problem by adding CO_2 to the water to change the acidity and thus limit the solubility of the SiO_2 from the masks. This predicament exists with wafers and is especially deleterious for those that have critical gate oxides. So, the hotter the water, the greater the extent of removal of metals and other materials, which is the good news. However, the hotter the water, the greater the removal of contamination from the vessel walls whether they are glass or plastic and greater will be the dissolution of the oxide on the wafer, which is the bad news.

In conclusion, when using water, it needs to be kept in mind that water is a chemical and has very extensive and unique properties. Furthermore, water acts not only as a solvent but as a medium for electrolytic reactions that involves not only the solvent and the solute but also the wafer. As water gets purer and hotter, the reactions need to be more seriously considered. It is also evident that the purer water becomes, the more it must be protected from the atmosphere from which it can absorb numerous contaminants, and from dirty vessels. The electrical characteristic of surfaces that water comes in contact with, the electrocapillary reactions of these surfaces, and the solubility of materials in UPW, hot or cold, must always be kept in mind. Whether water becomes a limiting factor in wafer production remains to be seen, but the problems that may

possibly occur need to be studied now, not only for the process engineer, but for the analytical chemist whose job it is to produce absolute quantitative numbers for accurate quality control.

Footnotes

1. Table is a modified version of Balazs Analytical Laboratory's "93 Pure Water Specifications and Guidelines for Facility and Fabrication Engineers," published June 1993. For a copy, please call Sally McKibben, 408-745-0600.
2. Chu, T. and Balazs, M.K., Semiconductor Pure Water and Chemical Conference, 1992, p241.
3. These Specifications and Guidelines were produced by Balazs Analytical Laboratory in 1988. In 1992, they were adopted by SEMI as Guidelines for the semiconductor industry. If one compares this Table to Table 1, the continued improvement in water quality can be seen.
4. Private communication concerning his work was given to the author with permission to publish the excerpts found in this paper. This includes Figures 1-3.

Table 1
SPECIFICATIONS FOR FINAL FILTER WATER QUALITY

TEST	ATTAINABLE	ACCEPTABLE	ALERT	CRITICAL
Resistivity @ 25°C	18.2	18.2	17.9	17.5
Particle/L by SEM				
0.1 - 0.2 μm	<200	<1000	>2000	-
>0.2 - 0.5 μm	<100	<500	>500	-
>0.5 μm	<1	<50	>100	-
Bacteria count/100mL				
by culture 100 mL sample	<1	<6	25	>25
1000 mL sample	<0.1	<1	-	-
by EPI	<10	<30	>50	>100
Silica (ppb)				
dissolved	<0.2	<1	>3	>10
total	<0.5	3	>5	>10
Residue (ppm) batch	<0.1	0.1	>0.1	>0.3
TOC (ppb) On Line	<1	<2	5	10
Ions (ppb) by Ion Chromatography				
Cations: Na ⁺	<0.01	0.05	>0.2	>0.5
K ⁺	<0.02	<0.1	>0.2	>0.5
NH ₄ ⁺	<0.06	0.1	>0.2	>0.5
Ca ⁺⁺	<0.02	<0.1	>0.1	>0.2
Mg ⁺⁺	<0.02	<0.1	>0.1	>0.2
Anions: F ⁻	<0.1	<0.1	>0.2	-
Cl ⁻	<0.02	0.1	>0.2	>0.5
Br ⁻	<0.02	<0.1	>0.1	>0.5
NO ₃ ⁻	<0.02	<0.1	>0.1	>0.5
NO ₂ ⁻	<0.02	<0.1	>0.1	>0.5
HPO ₄ ⁼	<0.02	<0.1	>0.1	>0.5
SO ₄ ⁼	<0.05	0.1	>0.2	>0.5

Table 2
SEMICONDUCTOR PURE WATER
SPECIFICATIONS AND GUIDELINES

Item	SPECIFICATIONS			GUIDELINES			
	Detection Limit**	256K DRAM		1M DRAM		4M DRAM	
		1985 Specs Attainable	1985 Specs Acceptable	1988 Specs Attainable	1988 Specs Acceptable	<1 μ VLSI	ULSI Target
Resistivity @ 25°C	18.2 max.	18.2	17.9	18.2	18.0	18.2	18.2
TOC (ppb)	5	<20	<50	<10	<30	<10	5
THM (ppb)	<1	—	—	—	—	<3	—
Particle / L by SEM	0.1-0.2 μ	—	—	—	—	<1500	<1000
	0.2-0.3 μ	—	—	—	<2000	<800	<500
	0.3-0.5 μ	—	—	<200	<200	<50	<10
	>0.5 μ	—	—	<1	<1	<1	<1
Particle / L by on-line laser	0.3-0.5 μ	<1	—	—	—	<50	<10
	>0.5 μ	<1	—	—	<100	<1	<1
Bacteria / 100mL	by culture	<1	0	<6	0	<6	0
	by SEM	—	—	<1	<10	<5	0
	by EPI	—	—	<5	<50	<10	<1
Silica-dissolved (ppb)	0.25	<3	<5	<0.4	4	3	1
Boron (ppb)	0.05	—	—	<0.05	2.0	0.005	*
Ions (ppb)	Na ⁺	0.05	0.05	0.2	<0.05	0.1	0.025
	K ⁺	0.1	0.1	0.3	<0.1	0.1	0.05
	Cl ⁻	0.05	0.05	0.2	<0.05	0.1	0.025
	Br ⁻	0.1	<0.1	0.1	<0.1	0.1	0.05
	NO ₃ ⁻	0.1	<0.1	0.1	<0.1	0.1	0.05
	SO ₄ ⁼	0.1	0.1	0.3	0.05	0.2	<0.05
	Ions total	0.5	<0.5	1.2	<0.5	<0.7	<0.2
	Residue (ppm)	<0.1	<0.1	<0.3	<0.1	0.1	<0.05

— Not available at this time
* Unknown
** With reasonable conc. where applicable

Table 3
Specifications and Guidelines

Item	SPECIFICATIONS				GUIDELINES		
	Detection Limit**	256K DRAM		1M DRAM		4M DRAM	
		1985 Specs Attainable	1985 Specs Acceptable	1988 Specs Attainable	1988 Specs Acceptable	<1 μ VLSI	ULSI Target
Metals (ppb) *							
Li	0.03	—	—	<0.03	0.05	0.003	
Na	0.05	0.05	2.0	<0.05	0.1	0.005	
K	.05	0.1	0.3	<0.05	0.1	0.005	
Mg	0.02	—	—	<0.02	0.05	0.002	
Ca	2	—	—	<2	<2.0	0.002	
Sr	0.01	—	—	<0.01	0.05	0.001	
Ba	0.01	—	—	<0.01	0.05	0.001	
B	0.05	—	—	<0.05	2.0	0.005	
Al	0.05	0.2	2.0	<0.05	0.05	0.005	
Cr	0.02	0.02	0.1	<0.02	0.05	0.002	
Mn	0.02	0.05	0.5	<0.02	0.05	0.002	
Fe	0.1	0.02	0.1	<0.02	0.1	0.002	
Ni	0.02	—	—	<0.02	0.05	0.002	
Cu	0.02	0.02	0.1	<0.02	0.05	0.002	
Zn	0.02	0.02	0.1	<0.02	0.05	0.002	
Pb	0.05	—	—	<0.05	0.05	0.005	

*Using ICP-MS, GFAAS, IC where required for lowest level of detection. These elements represent the metals that are usually found in ultrapure water.

Table 4
COMPARISON OF ELECTRONIC GRADE
WITH ULTRA PURE NITRIC ACID

CHEMICAL 70% NITRIC ACID	ELECTRONIC GRADE	ULTRAPURE
Aluminum	1.1	<0.5
Antimony	<0.1	<0.01
Arsenic	<0.2	<0.1
Barium	0.1	<0.05
Beryllium	<0.1	<0.005
Boron	3.0	≤3
Cadmium	<0.1	<0.005
Calcium	3.0	0.5
Chromium	0.2	0.02
Cobalt	<0.05	<0.05
Copper	0.4	≤0.05
Gallium	<0.05	<0.1
Germanium	<0.1	<0.1
Gold	<2.0	<0.005
Iron	2.1	<0.5
Lead	0.2	0.005
Lithium	<0.05	<0.01
Magnesium	1.3	<0.09
Manganese	<0.1	<0.005
Molybdenum	<0.05	<0.02
Nickel	0.1	≤0.1
Potassium	<3.0	<2
Silicon	12	<2
Silver	<0.1	<0.005
Sodium	6.8	<2
Strontium	<0.05	<0.005
Tin	<0.05	<0.01
Titanium	<0.5	<0.05
Vanadium	<0.1	<0.005
Zinc	0.5	<0.06

Figure 1: Rinse of Ta, La and Bi in ICP-MS
pneumatic nebulizer system

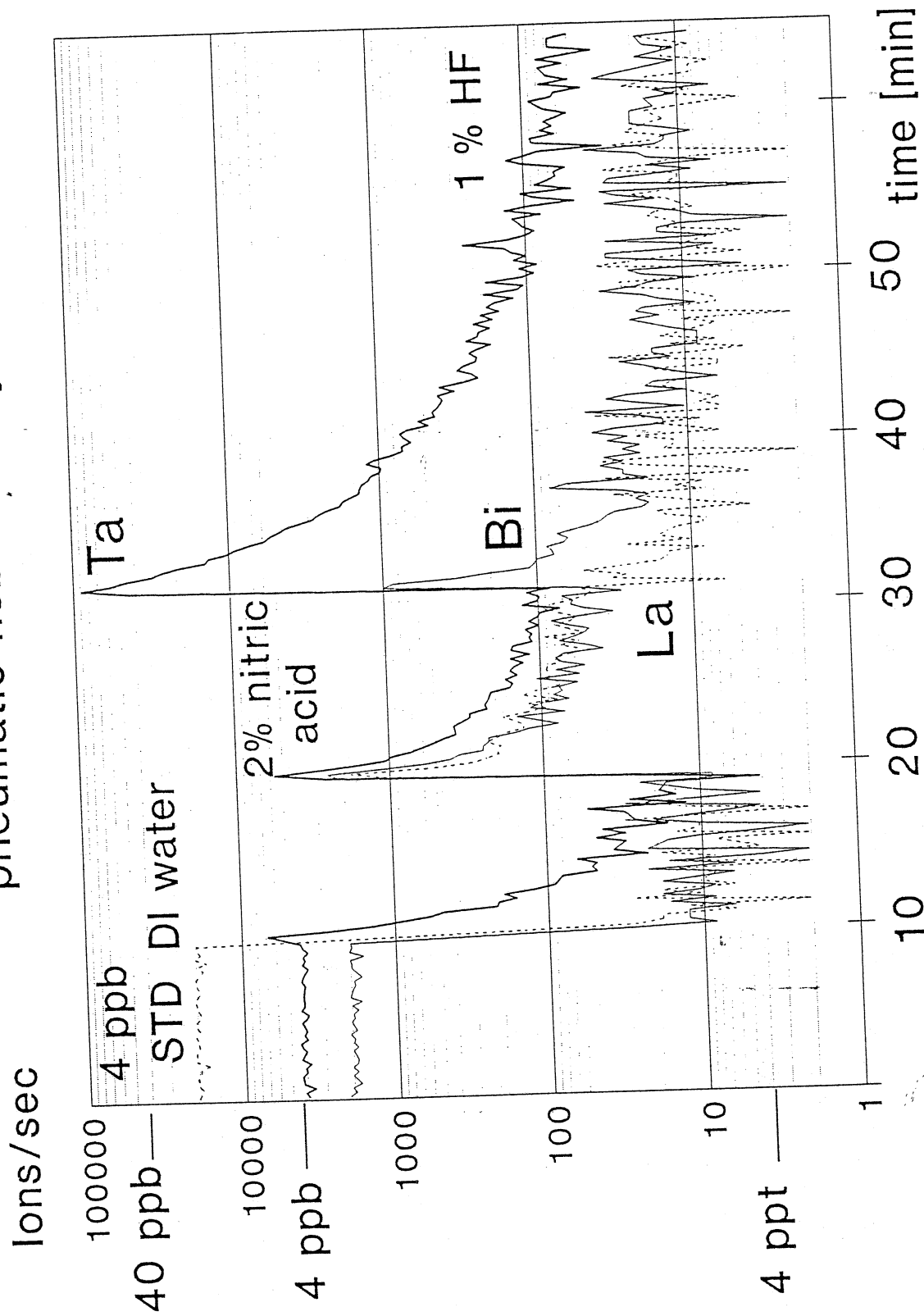


Figure 2: Rinse of niobium in ICP-MS
pneumatic nebulizer system

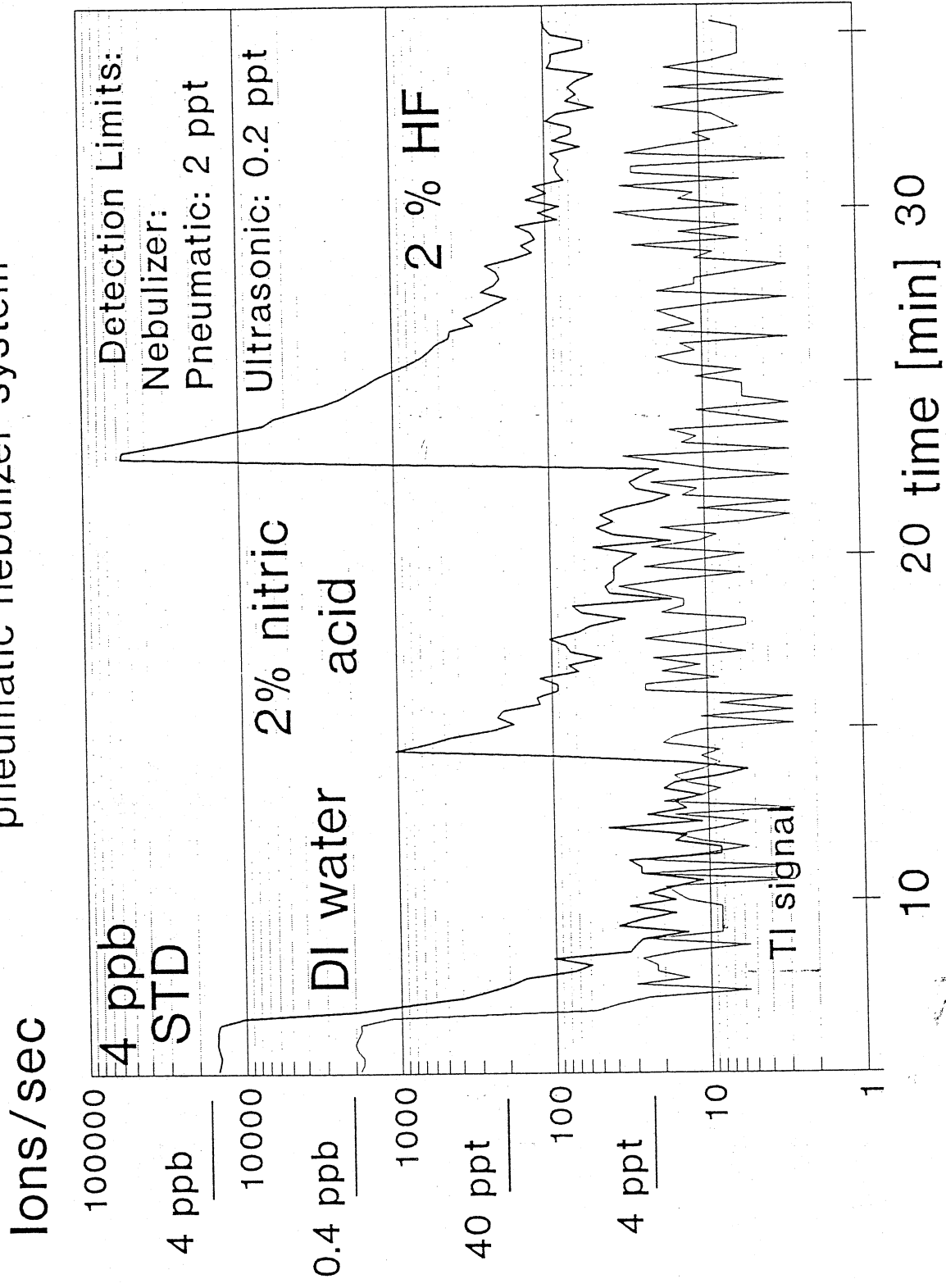


Figure 3: Rinse of indium and iridium in ICP-MS
pneumatic nebulizer system

