A New NonVolatile Residue Monitor for the Semiconductor Industry

David Blackford, PhD., Fluid Measurement Technologies, Inc.

Introduction

Nonvolatile Residue (NVR) consists of dissolved inorganic material. NVR is primarily silica (both in dissolved and colloidal forms) but also includes sodium, anions, cations and trace metals. Nonvolatile Residue is **not** particles.

The ability to measure Nonvolatile Residue is significant because NVR can be used as a measure of overall water quality. Significant amounts of NVR indicate a possible problem with an ultrapure water supply - in fact, NVR is often the first on-line measurement and therefore the first indicator of a problem in a UPW system. With the NRM Model 8000, NVR can be measured at ppt levels in almost real-time.

As with other on-line TOC monitors and particle counters, the Model 8000 NRM does not identify the residue. However in industries such as Semiconductor manufacturing, fast identification of contamination is critical.. The primary advantage of the NRM comes from the fact that it gives an almost immediate indicator of the presence of contamination. After the speedy indication of a problem, the technician can then collect and analyze a water sample to identify the contaminant.

Many facilities continue to manufacture semiconductors without measuring NVR. However, as semiconductor line-widths become smaller, the manufacturing process will become more susceptible to contamination. The ITRS Roadmap committee is working to find parameters to measure at the required detection limit. For future semi-conductor manufacturing, measuring NVR may give a critical advantage.

History of the NRM

Twenty years ago, Bob MacIntosh was interested in finding a way to detect colloidal silica in ultrapure water (UPW) in near real-time. At that same time Intel was experiencing hazing problems on their final wafers. Intel attributed the hazing to colloidal silica in the final rinse water. Colloidal silica is very difficult to remove from UPW and almost impossible to detect.

In the meantime, Dr. David Blackford was involved in a project measuring the particle size of carbon black used in tire manufacturing. The technique used involved suspending the carbon black in “pure water,”and then nebulizing the suspension. The nebulized droplets were dried to recover the carbon black and finally the carbon black was sized with a sub-micron particle sizer. However, the particle sizer always showed two peaks: A large peak that corresponded to the expected size of the carbon black and a second, much smaller, “mystery” peak. The second peak could be controlled by the quality of the water used for the carbon black suspension, therefore Dr. Blackford concluded that the mystery peak was produced by the water And that he had stumbled across a technique for measuring water quality.

Bob Macintosh asked Dr. Blackford if he knew of a way to detect colloidal silica in near real-time in ultrapure water and the response, based on the carbon black experiment discovery, was “Yes.”.

In fact, Dr. Blackford was not the first to suggest this technique for measuring water quality – it was first suggested by two Australian professors, Salkowski and Werle, who built an instrument that measured nonvolatile residue in solvents. (Salkowski and Werle, 1964) The Salkowski and Werle instrument is shown in Figure 1. However, after building the instrument, the technique appears to have been totally ignored for the next 25 years. It took the emergence of the semiconductor industry, and that industry’s almost insatiable demand for ever cleaner ultrapure water, to provide the impetus to develop the technique. Dr. Blackford developed the original Nonvolatile Residue Monitor to meet the semiconductor industry’s need. In 2007 Dr. Blackford further refined the design of the NRM and released a new, improved model.

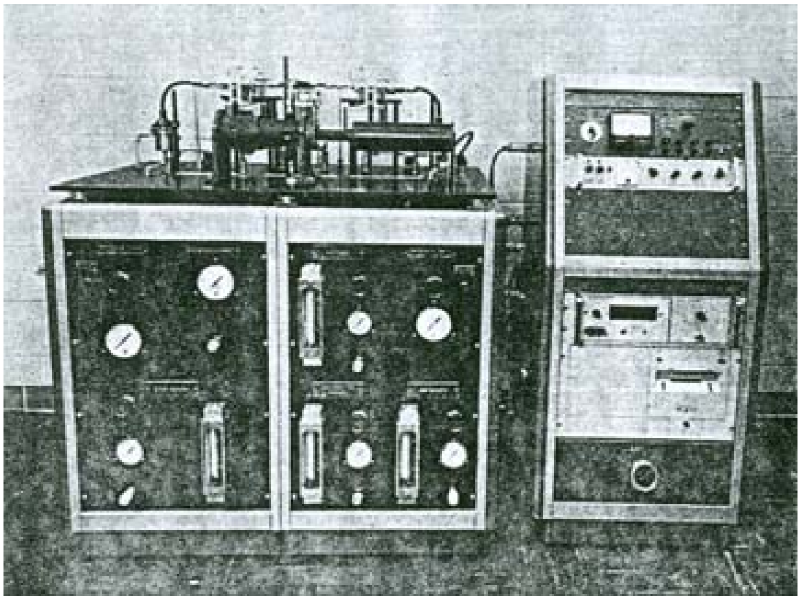

Figure 1: Salkowski and Werle Water Quality Instrumentation.

How the NRM Works

Overview

The NRM monitors ultrapure water quality continuously, in real-time, by measuring the amount of Nonvolatile Residue After Evaporation (RAE). Water flowing into the NRM is nebulized to create droplets. The droplets are then dried to create a residue and the residue particles are counted.

The most recent version of the NRM has been updated to include modern electronics and a Water-based Condensation Particle Counter (WCPC). The WCPC replaced the original alcohol-based CPC and is ideally suited as the “engine” for the new NRM for the following reasons:

- No external water reservoir is needed - the WCPC uses ultrapure water (the same water the NRM is monitoring) instead of alcohol.
- The measurement range is wider than that of the alcohol-based CPC and no longer requires the use of diffusion screens.
- By using less internal tubing, and eliminating most of the diffusion losses, the response time is almost ten times faster than the original NRM.

Figure 2 is a schematic diagram of the most recent NRM.

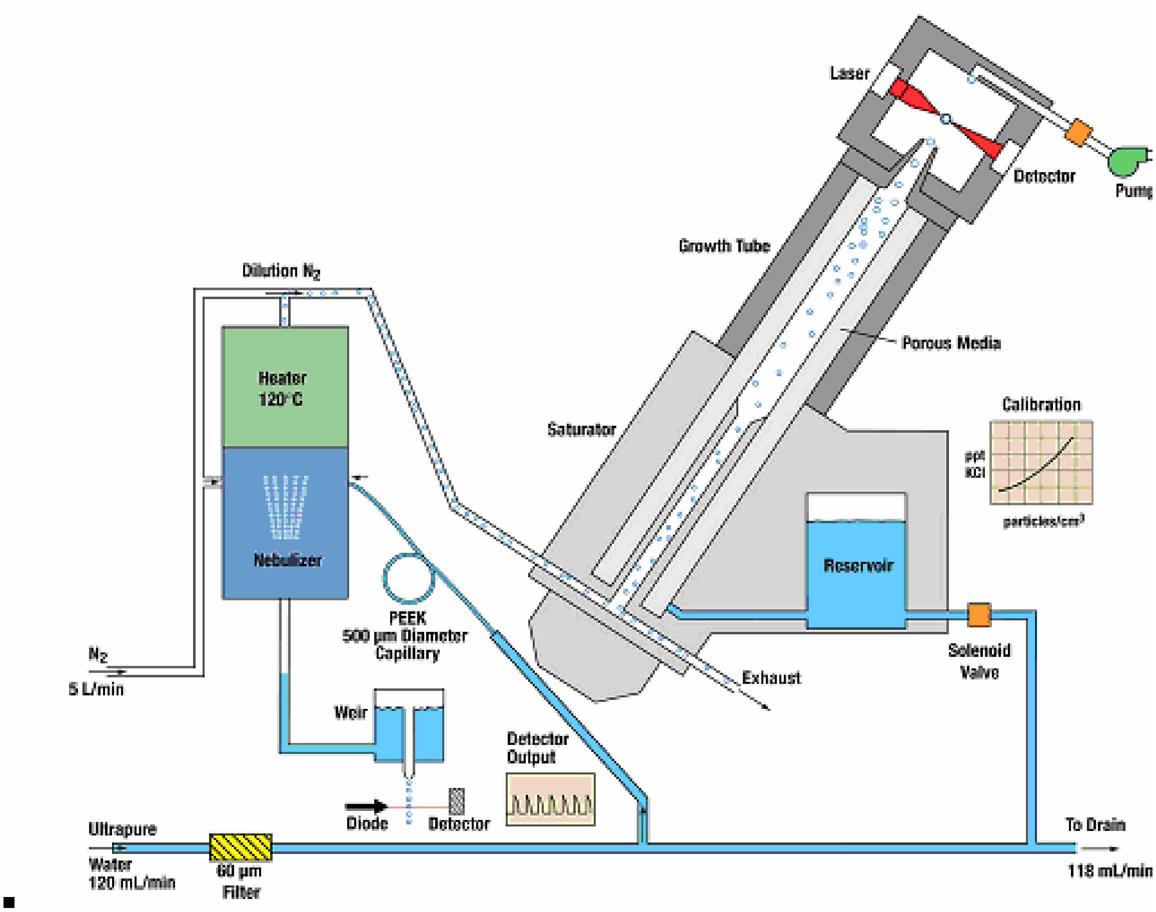

Figure 2. NRM Schematic Diagram

Nebulizing the Water Flow

Water at approximately 120 mL/min enters the NRM through a connection on the back panel of the NRM. After passing through a sintered stainless steel filter (60 µm pore size) to remove any large debris in the water, water flows to an air-actuated pressure regulator. Adjusting the air pressure to the regulator automatically adjusts the water pressure. The water pressure reading can be read as a digital display (in psi) on the front panel. Using an air-actuated pressure regulator eliminates the potential of internal leaks if somebody inadvertently turns off the air supply (the water pressure regulator closes and prevents water from entering the NRM).

After the pressure regulator and pressure transducer, a tee fitting delivers water to the nebulizer through a section of PEEK microbore tubing. The PEEK tubing gradually reduces the water pressure and prevents any out-gassing of dissolved gases in the incoming water. Within the nebulizer, water and a source of compressed air, or nitrogen, both supplied at constant flow rate and pressure, combine to form a stable, poly-dispersed aerosol of ultrapure water droplets.

Residue Particle Creation and Counting

Ultrapure water droplets produced by the nebulizer are rapidly heated at 120°C. Each water droplet is evaporated to dryness, leaving behind a particle of residue consisting of dissolved inorganic material. Every atomizer droplet will result in a residue particle, no matter how clean the ultrapure water. However, the cleaner the ultrapure water, the smaller the amount of residue within each droplet, and the smaller the resulting residue particle. After the heater, additional compressed air, or nitrogen, is introduced to prevent re-condensation and quickly move the residue particles to the Water-based Condensation Particle Counter (WCPC).

The WCPC uses a patented technology where water is used as the working fluid without the requirement of mixing or adiabatic expansion techniques. A condensation technique deposits a working fluid on the residue particles to grow (amplify) their size to a value that can be detected readily with a conventional optical system. The stream of residue particles is uninterrupted and follows a laminar-flow path from the sample inlet to the optical detector.

The residue particles enter the sample inlet and immediately half of the inlet flow is extracted, filtered, and then combined with the remaining sample flow as clean sheath air. This combined flow enters a region surrounded with wetted media. The stream of residue particles is saturated with water vapor and the temperature is equilibrated. The residue particles then pass to a growth section where the wetted walls are heated to produce an elevated vapor pressure. The high diffusivity of the water vapor allows the vapor to reach the center of the sample stream at a faster rate than the thermal diffusivity of the vapor can equilibrate to the higher temperatures near the walls – creating a supersaturated condition along the radius of the flow stream. Residue particles in the flow stream act as nuclei for condensation - water continues to condense on the residue particles as they pass up the growth tube. The enlarged residue particles are then detected by the optical detector. The clean sheath air is used in this system to keep the residue particle sample flow in the center of the growth tube where super-saturation is the highest.

Like all particle counters, the WCPC has its lower detection efficiency defined by a curve ranging from 0% efficiency (at some size), to 100 % efficiency (at a larger size). Figure 3 shows a typical detection efficiency curve. The 50 % efficiency point occurs at approximately 6.5 nanometers - half the particles at 6.5 nm act as sites of nucleation for subsequent particle growth in the WCPC's supersaturated water vapor, and half do not.

The nebulizer produces a Gaussian size distribution of residue particles, shown in Figure 3 superimposed on top of the detection efficiency of the WCPC.

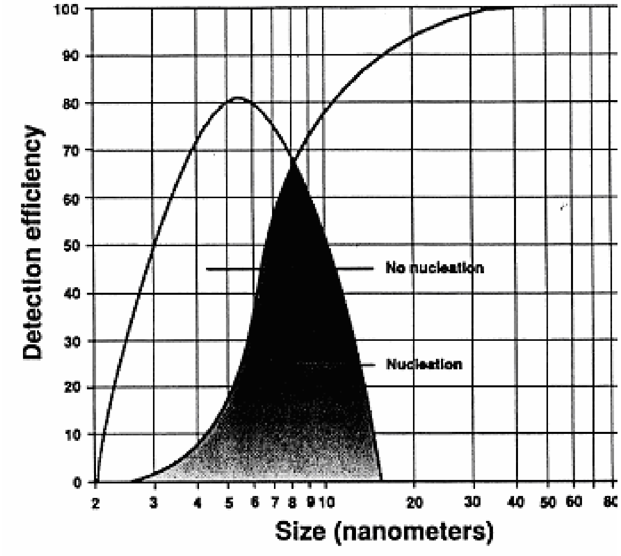

Figure 3: WCPC Detection Efficiency Curve of the WCPC Superimposed on the Gaussian Size Distribution of Residue Particles.

Particles to the left of the WCPC's efficiency curve do not initiate nucleation, and therefore are not counted by the WCPC. Particles to the right of the efficiency curve act as sites for nucleation and therefore are counted. If the ultrapure water becomes "dirtier," or if the water contains an increased level of KCl during calibration, each droplet from the nebulizer remains the same size, but contains more residue. Therefore, when the ultrapure water droplet dries, the resulting residue particle is larger. The Gaussian size distribution of the residue particles therefore shifts to the right when superimposed on top of the WCPC's efficiency curve as shown in Figure 4.

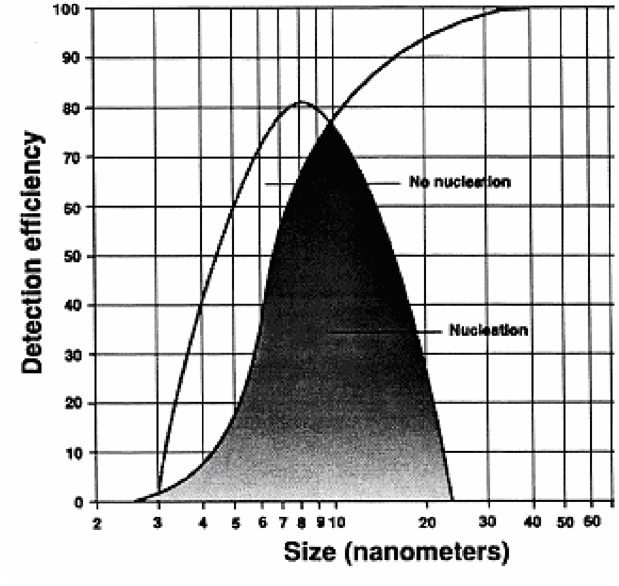

Figure 4: The Gaussian Size Distribution Moves to the Right as the Water Becomes more Contaminated.

NRM Calibration

The residue particle concentration from the WCPC must be equated with parts per trillion (ppt) of contamination - achieved by calibrating with known amounts of potassium chloride (KCl). KCl is an ideal compound for calibrating the NRM because in its dry form, KCL:

- Has a purity level > 99.98%.
- Is non-toxic.
- Has a density that approximates to silica, one of the primary sources of nonvolatile residue found in ultrapure water.

During the calibration procedure, KCl is added to ultrapure water just upstream of the NRM using a custom-designed, motorized, syringe injection system. A typical calibration for 1ppb, 2ppb and 3ppb challenges for KCl is shown in Figure 5. Note the fast response time to changes in the KCl challenges and the equally fast clean-up once the challenge is discontinued.

The motorized syringe technique means the flow of water through the NRM is uninterrupted and the background impurity level is kept to a minimum. A calibration curve is plotted using a minimum of ten calibration points (ten points are necessary to accurately calibrate the NRM over its operating range). When the calibration curve is plotted, approximately 20 points (spanning the NRM's operating range) are loaded into the NRM's Electrically Erased Programmable Read Only Memory (EEPROM).

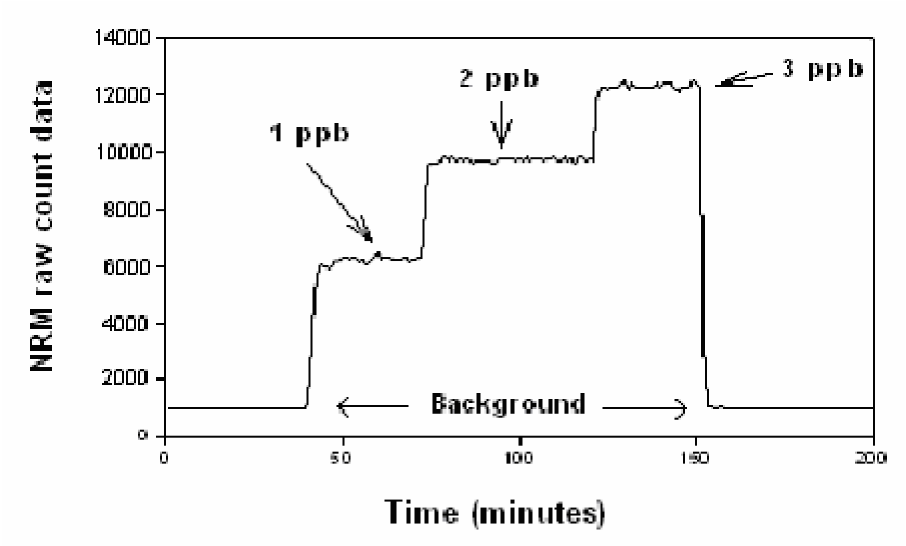

Figure 5: NRM Response to three different KCl challenges.

Figure 6 shows the NRM's response to two sequential challenges of 9.8 ppt of KCl. Signal-to-noise ratio is about 10:1. Even at these very low-level challenges, the KCl peaks are clearly defined. Ongoing refinements to the new NRM technology may mean that eventually a version measuring ppq (parts per quadrillion) will be available.

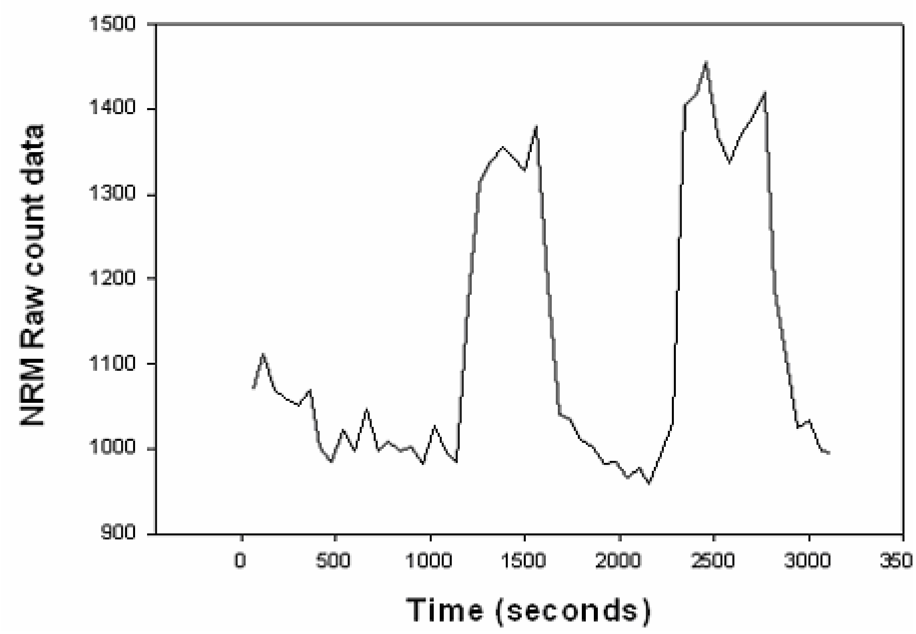

Figure 6: NRM Response to a 9.8 ppb KCl Challenge.

Measuring the Flow Rate through the Nebulizer

The original NRM used a conventional flowmeter to measure the incoming flow rate to the nebulizer. Reading the flow rate from this flowmeter was difficult since the flowmeter could only be accessed from the back of the instrument. This conventional method of measuring flow rate with a flowmeter also risks adding an additional source of contamination to the water supply.

Incorporated into the updated NRM is a new, patented method of measuring the flow rate of water flowing through the nebulizer. The new method incorporates the following steps:

1. 95% of the water delivered to the nebulizer leaves the nebulizer as a waste stream. The waste water is collected by a weir and stand-pipe system to deliver a steady stream of waste water droplets.
2. The droplets, identical in size, fall through a simple light beam. As each droplet breaks the beam, the detector senses a scattered light signal, or pulse, and a counter keeps track of the pulses.
3. An algorithm converts the pulse count to a flowrate in mL/min, The count is displayed on the front panel of the NRM. Both the nonvolatile residue level in ppt, and the flowrate through the nebulizer in mL/min, are updated every second.

With this improved method, no external source of contamination is possible and the new digital readout is readily visible on the front panel.

Practical Applications

Dissolved silica

Figure 7 is a graph showing results of simultaneous data collection for both NVR and a conventional Dissolved Silica Monitor at a US semiconductor facility. Just after midnight, the Silica Monitor records a spike and then the data returns to indicating background readings. In contrast, NVR values recorded by the NRM show the disturbance at midnight, but then continue to record the water quality excursion for another six hours. The event recorded here was probably routine UPW maintenance, scheduled for midnight when water usage was at a minimum. UPW Operators will typically ignore a spike such as the one recorded by the Silica Monitor because it is shown as a single event. However, in the future, events such as this may have a significant impact on production and will no longer be able to be ignored.

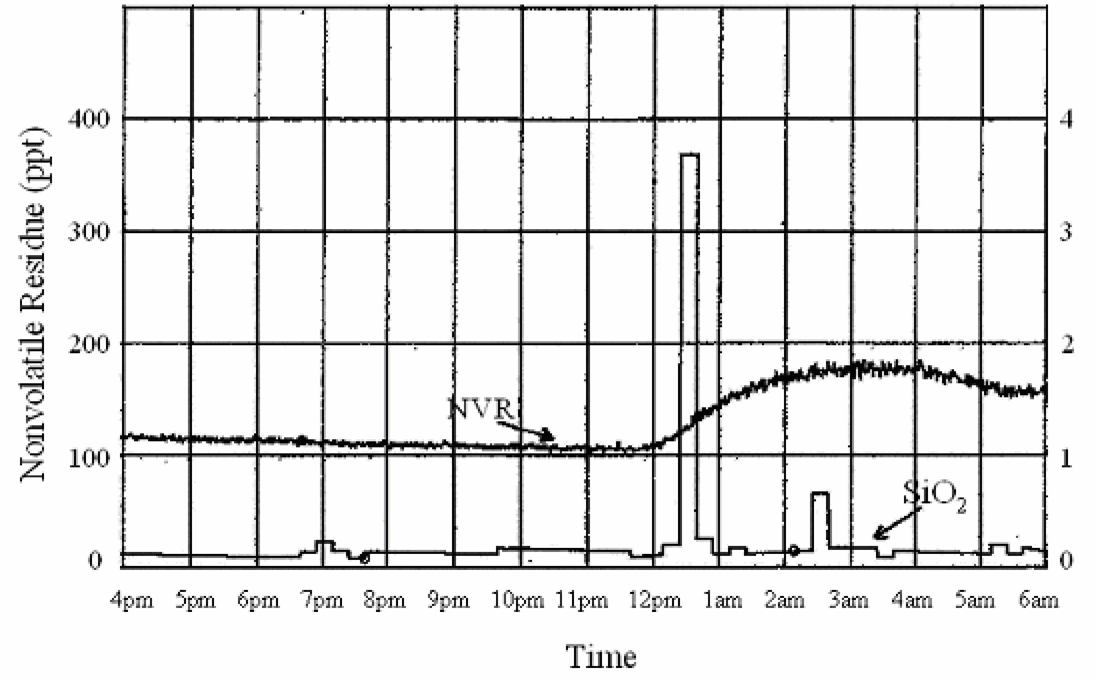

Figure 7: Simultaneous data collected for the NRM and a conventional Dissolved Silica Monitor.

Filter testing

The new NRM is currently being used by a US filter manufacturing company to develop new filters for the semiconductor industry, with a goal of developing a new filter test standard for nm pore size filters for use in semiconductor manufacturing. The filters under development should be capable of removing nm sized particles.

Figure 8 shows a low-level colloidal silica (22 nm) challenge passing through a 20 nm pore size test filter and by-passing the test filter. This test could not be performed with the current standard challenge of Polystyrene Latex (PSL) spheres and an optical particle counter. The sensitivity of the NRM is such that a very low level challenge (< 10 ppb) can be used, therefore the test filter does not become loaded with colloidal silica. The rapid response time of the NRM allows for challenges of short duration. These two factors are critical when testing filter performance – an ideal test must have as little effect on the filter as possible. The NRM facilitates short testing and testing with a low concentration of the challenge material. Efficiency for the test filter shown in Figure 8 was measured at 72%.

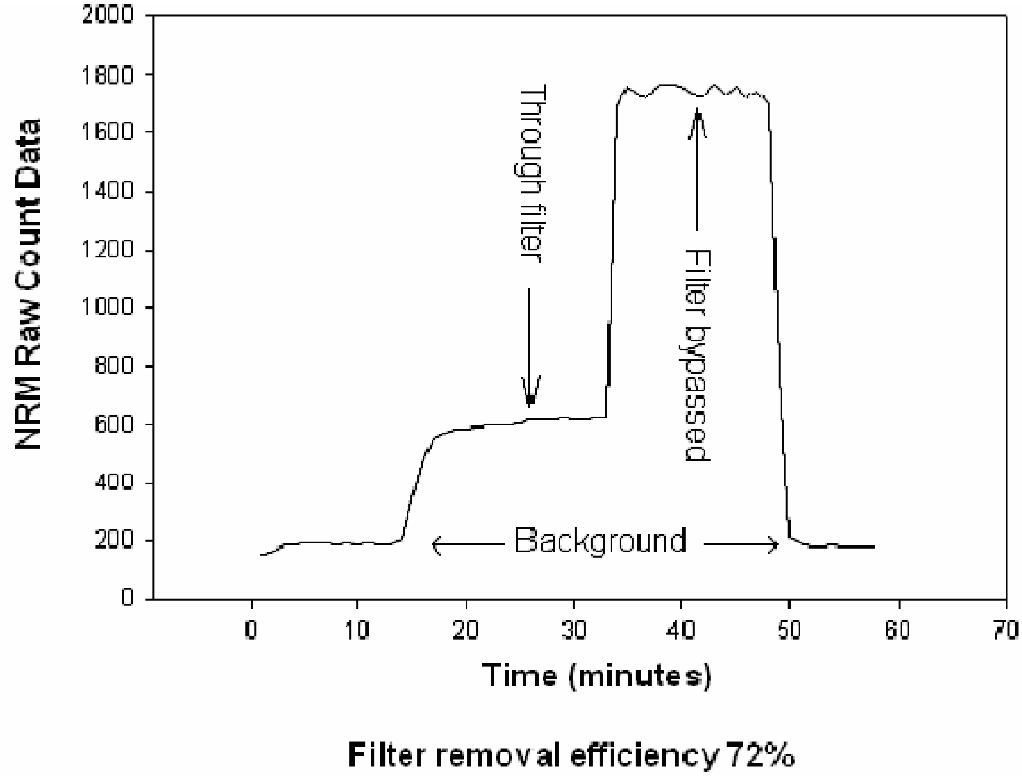

Figure 8: Low level (< 10ppb) 22nm Colloidal Silica Challenge through a 20 nm Pore Size Filter.

International Technology Roadmap for Semiconductors (ITRS)

In 2007, the NRM was part of a "Round Robin" exercise for the ITRS 2007 UPW update. The NRM was one of the instruments used to collect data for the following parameters:

- Particles by SEM
- TOC
- Ions
- Trace Metals
- Dissolved Oxygen and dissolved nitrogen
- NVR

Samples were collected at either Point of Entry (POE) to equipment or sub-equipment, or at Point of Use (POE) at the process chamber. A total of 6 US sites were chosen. The NVR data is shown below in the order of highest to lowest values – it shows a significant difference in NVR values among the sites. .

Site	NVR
Site A	245 ppt
Site B	243 ppt
Site C	199 ppt
Site D	150 ppt
Site E	102 ppt
Site F	96 ppt

Table 1: ITRS NVR Data.

Conclusions

While the original NRM offered a new method of contamination monitoring for UPW, the new NRM builds upon that method by incorporating significant design and technology improvements. The flammable solvent used as the working fluid for the CPC is no longer necessary and has been replaced by ultrapure water, the same ultrapure water the detector is monitoring. The detection level is currently 1ppt and a ppq NRM is in the near future.

References

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2. Salkowski, M.J. and Werle, D., “Non-Volatile Residue Nephelometer”, Proceedings of Surface Contamination Symposium, Gatlinberg, TN., June 1964.
3. Hering, S.V. and Stolzenberg, M.R., US Patent Number 6,712,881 “Continuous, laminar flow water-based particle condensation device and method”, issued March 30, 2004.