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ABSTRACT

A Nonvolatile Residue Monitor (NRM) has been developed for continuously monitoring Residue After Evaporation (RAE) in high-purity water. Until recently, the only method for measuring nonvolatile residue was to slowly evaporate one liter of water and then make a gravimetric determination of nonvolatile residue. This evaporation process can take several hours and provides a lower detection level of 100 ppb at best.

Our technique is based on the principle of determining RAE of atomized droplets. Since droplets evaporate in seconds, each droplet leaves an ultrafine nonvolatile residue particle agglomerate; the size of which is related to the amount of residue impurity originally present in the liquid. A Condensation Particle Counter (CPC) then monitors the concentration of ultrafine nonvolatile residue particles. The CPC output is calibrated to give a readout in ppb by weight of potassium chloride. The measurement range of this technique is 0.01 ppb to 20 ppm.

This paper describes our technique in detail and provides several case studies where the measurement of nonvolatile residue has provided unexpected results.

INTRODUCTION

The quality of ultrapure water used to manufacture semiconductors is becoming more critical as line geometry continues to shrink. Some of the most challenging semiconductors to manufacture are "dynamic random access memory" devices (DRAMs). DRAMs with 256-megabit capacity (line widths at 0.25 μm) and one gigabit capacity (line widths at 0.15 μm) will be in production within the next 5 years. Semiconductor fabrication involves 70 or more stages of chemically processing the surface of a single wafer of semiconductor material. Between each stage of the processing, chemicals used in the previous stage must be thoroughly washed from the wafer's surface with ultrapure water. Thousands of liters of ultrapure water may be used in processing a single wafer. Impurities in the water, whether dissolved (compounds of organic or inorganic materials) or in suspension (particles or colloidal material), can remain on the wafer's surface after washing and potentially cause defects in the resulting semiconductor device. It is therefore imperative to use water of the highest purity to limit, or eliminate, defects.

Engineers responsible for today's ultrapure water systems need to use a variety of on-line and off-line measurement techniques in order to maintain water systems. A new technique has recently been developed for the on-line measurement of nonvolatile residue. This technique offers process water engineers an additional tool to optimize the performance of ultrapure systems and investigate individual system components. The technique is based on the principle of determining the RAE of atomized liquid droplets. Each droplet rapidly dries to leave an ultra-fine, nonvolatile residue particle whose size is related to the amount of residue impurity originally present in the liquid. The measurement of nonvolatile residue can be thought of as an overall measurement of water quality; however, as nonvolatile residue is non-specific, the source of the residue cannot be identified. The current lower detection limit for nonvolatile residue is 0.01 ppb.

AN HISTORICAL PERSPECTIVE

The first attempts to measure nonvolatile residue in solvents in real time by the atomization/drying/residue detection technique were made by Ford and Kennard [1] and Salkowski and Werle [2]. Both used an atomizer, a drying column to evaporate the solvent, and a light-scattering device to detect the resulting particles of residue. Both instruments could measure nonvolatile residue with a lower detection level of about 50 ppm. Niida *et al.* [3] and Blackford *et al.* [4] described an instrument that retained an atomizer, but replaced the light scattering device with a much more sensitive CPC. Nonvolatile residue levels as low as ten ppb could now be measured. Blackford has since improved the detection technique to allow a lower detection level of ten ppt. In 1994, the measurement technique described in the paper became the ASTM "Standard Test Method for On-Line Measurement of Residue After Evaporation of High-Purity Water," designated D 5544-94.

THE MEASUREMENT TECHNIQUE

Figure 1 is a schematic diagram of the components of the NRM. An atomizer, supplied with ultrapure water at a constant flow rate, and a source of high-pressure compressed air or nitrogen, filtered through a HEPA filter at a constant flow rate and pressure, combine to generate a stable aerosol of ultrapure water droplets. The ultrapure water droplets enter a drying column and are rapidly mixed with dried, filtered, heated (at 120°C), compressed air or nitrogen. The droplets dry rapidly, probably within the first few centimeters of the drying column. Every atomizer droplet results in a residue particle, regardless of water quality. However, the cleaner the ultrapure water, the smaller the residue particles. As the nonvolatile residue particles emerge from the drying column, a small percentage are removed and passed through a diffusion screen before being counted by a CPC.

Diffusion screens filter small particles by virtue of weak Brownian motion forces. Larger particles are unaffected by Brownian motion forces and pass straight through the diffusion screen. A diffusion screen therefore preferentially removes small particles and effectively shifts the detection efficiency of the CPC to larger sizes. Changing the mesh size of the diffusion screen, and the number of diffusion screens is an easy and convenient way of changing the residue monitor's measurement range from ten ppt to twenty ppm.

In the CPC, n-butyl alcohol vapor condenses onto the surface of the nanometer-sized residue particles. Residue particles of a certain size and above act as nucleation sites for the alcohol, resulting in particle enlargement. Particles grow to a uniform size that can then be counted with a relatively simple optical particle counter. As the ultrapure water becomes more contaminated, the number of residue particles able to initiate nucleation increases and the CPC counts more particles. The CPC measures particle concentration in units of particles/cm^3. A calibration technique is therefore required to equate the CPC's measurement with ppb by weight for nonvolatile residue.

Within the NRM, internal sources of contamination are kept to a minimum by the use of certain materials. The atomizer is machined from 316 stainless steel that is passivated to render the surface non-reactive. The delivery tubes and fittings are made of persfluoroalkoxy (PFA) Teflon. To further reduce potential sources of contamination the NRM does not have an internal pump; external water pressure feeds water into the NRM instead. An internal flow controller ensures an adequate flow rate of water (approximately 70 ml/min) flows through the instrument.

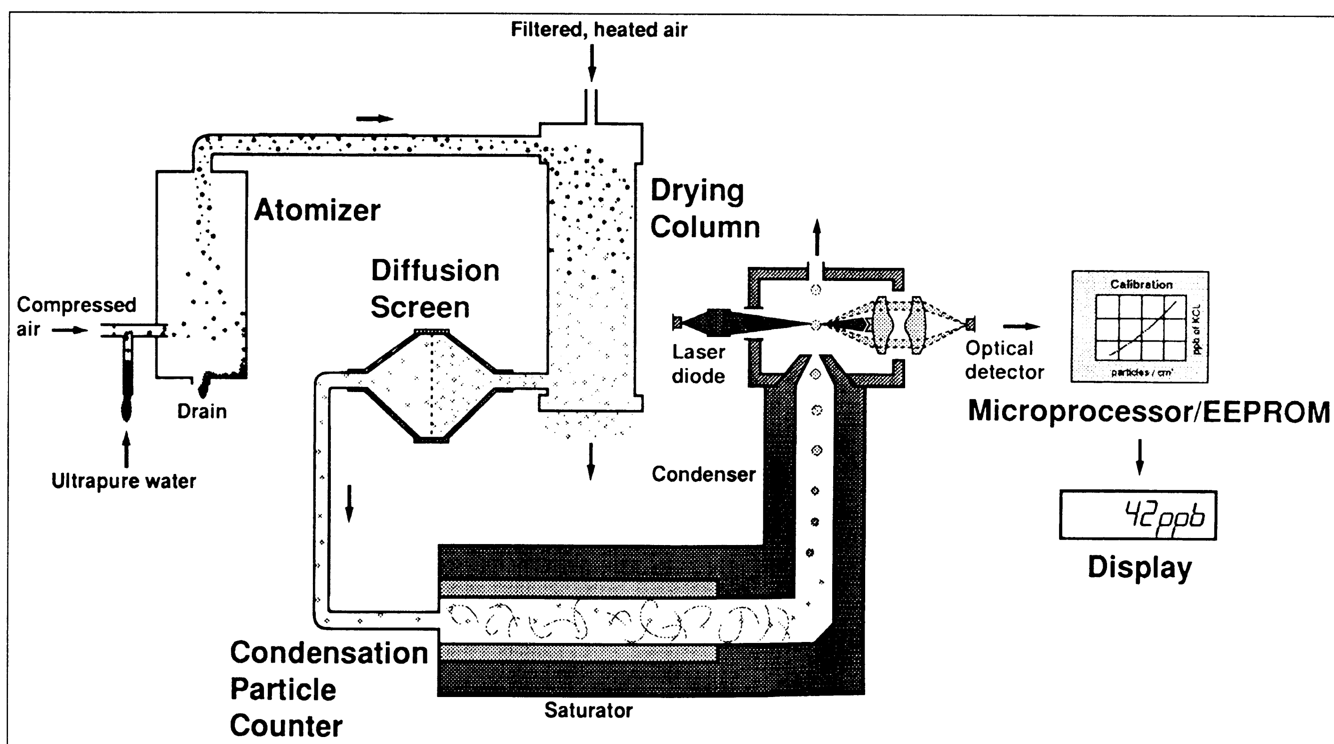

Figure 1. Schematic diagram of the Nonvolatile Residue Monitor.

CALIBRATING THE NRM

A schematic of the setup used to calibrate the NRM is shown in Figure 2. A motorized syringe injection system introduces a controlled amount of potassium chloride (KCl) at a constant rate into the ultrapure water flowing through the NRM being calibrated. Atomic Absorption Spectroscopy (AAS) is used to verify the concentration of potassium in the ultrapure water. The flow of ultrapure water through the NRM is not interrupted during calibration. We use a 60 ml polypropylene syringe, large enough to allow several hours of uninterrupted operation. Tests have shown that the syringe itself introduces negligible amounts of residue impurity. After each injection, any residual KCl is rapidly flushed away, making the instrument ready for the next injection.

The KCl solutions are made by weighing dry, 99.98% KCl and dissolving it into a known volume of ultrapure water. Typically, ten different levels of KCl are sequentially introduced during a calibration run. Each KCl concentration (calculated from the weight of KCl and the known dilution) is allowed to stabilize, and the reading in particles/cm^{-3} is recorded. The stopcock is opened and a sample of the KCl solution is withdrawn for AAS analysis. The AAS measurement is used to check that the dry KCl weight and subsequent dilution in ultrapure water has been accurately performed.

Using this method, a series of calibration points can be plotted and a regression analysis used to produce a calibration curve (see Figure 3) relating the CPC output in particles/cm3 to an equivalent KCl ppb by weight. The calibration curve is loaded into the CPC's Electrically Erased Programmable Read Only Memory (EEPROM) enabling the CPC to display a readout of nonvolatile residue in ppb.

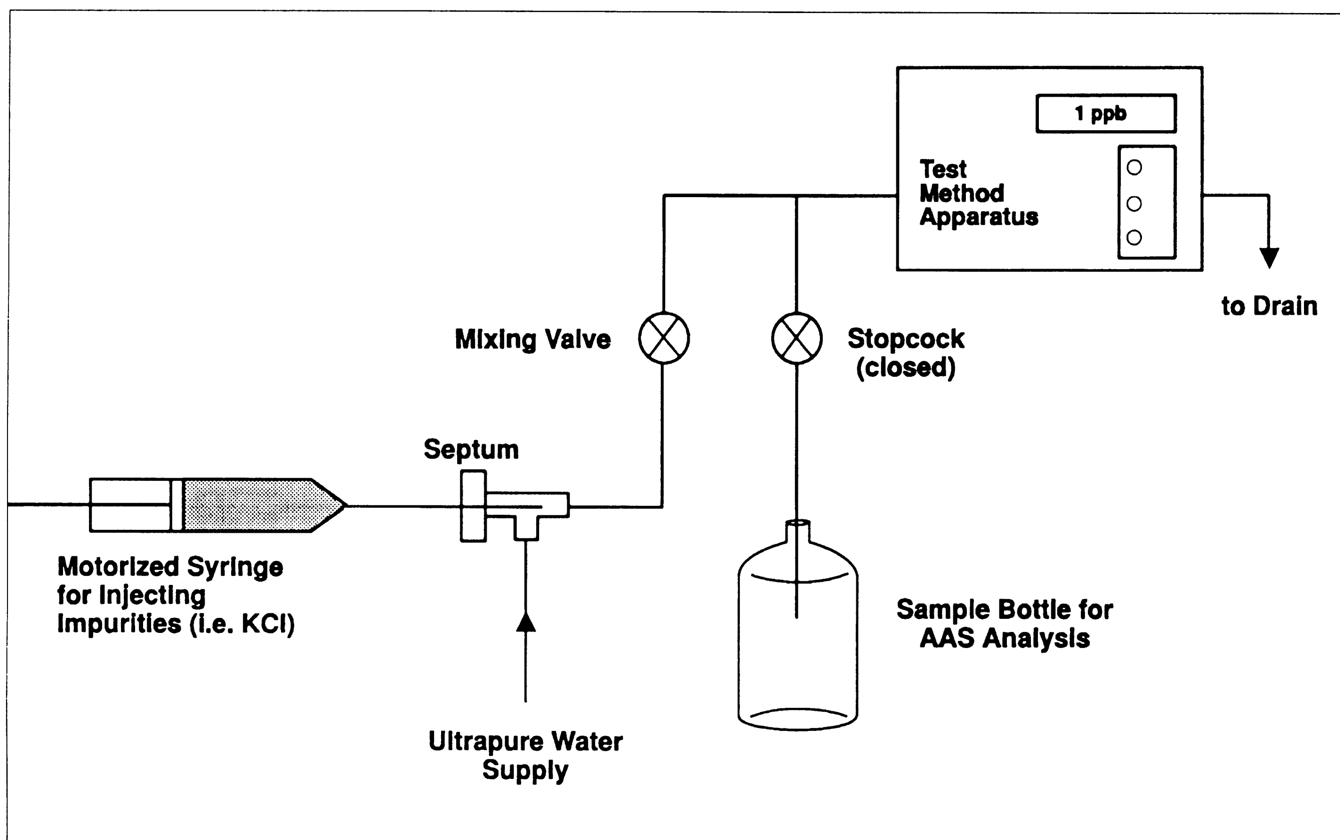

Figure 2. Schematic of the NRM's calibration setup.

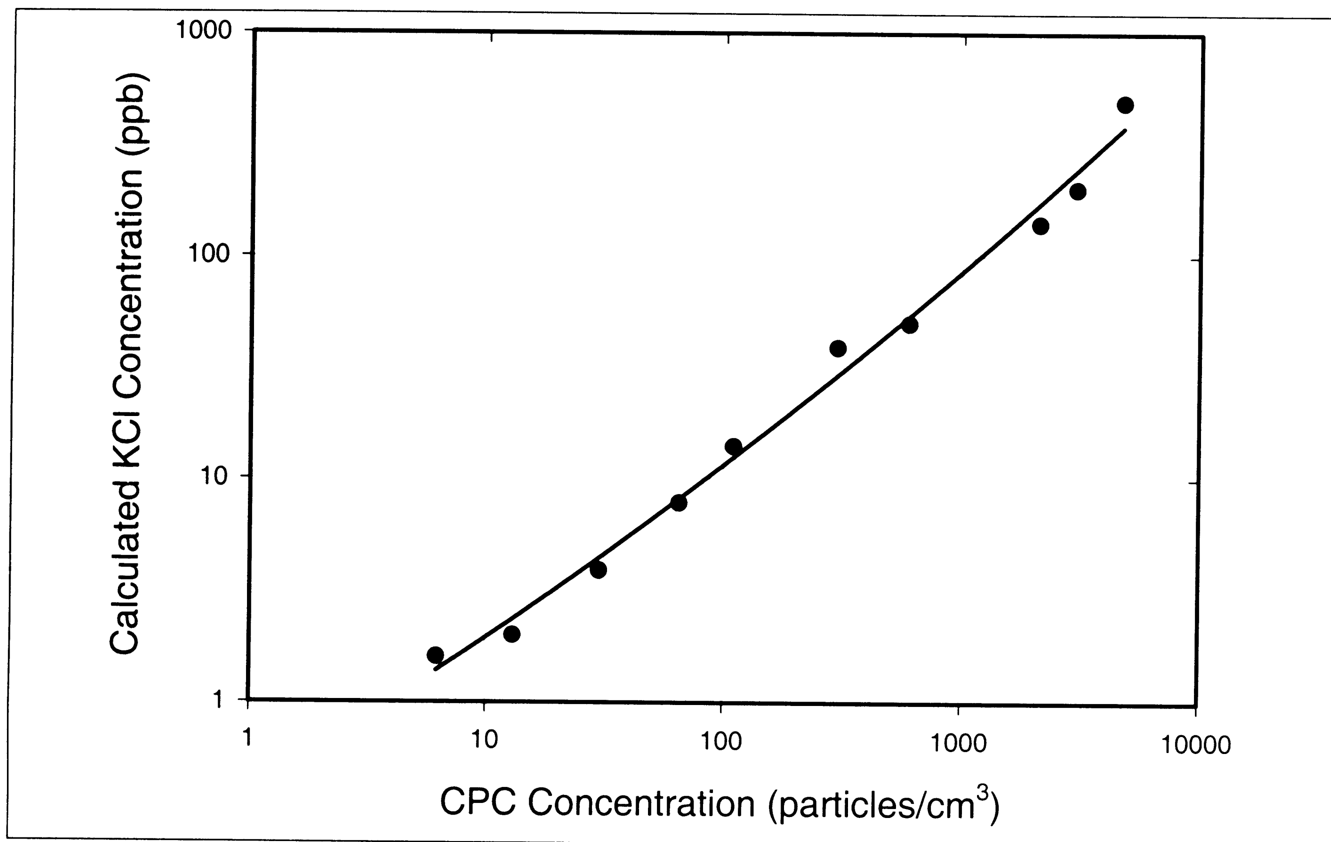

Figure 3. Typical NRM calibration curve.

CASE STUDY 1

Residue measurements were made before and after a bank of final filters (0.2 μm pore size) at a facility that manufactures silicon wafers. The filters were suspected of adding some contaminant to the water supply, but an on-line TOC monitor and a resistivity monitor measured the same levels of TOC and resistivity upstream and downstream of the filters. A particle counter indicated that the filter was doing a good job of removing particles. However, the NRM (see figure 4) measured a much higher level of contamination downstream of the filter than before the filter. This result clearly indicates that the filters and/or the filter housing were adding significant non-volatile contamination to the quality of the final water.

CASE STUDY 2

The measurement of resistivity has traditionally been relied upon to monitor breakthrough on an ion-exchange bed. However, resistivity can only detect dissolved inorganic charged ions. When an ion-exchange bed initially exhausts, it is the weakly charged, dissolved silica and colloidal silica that are preferentially released, neither of which can be detected by measuring resistivity. To better detect ion-exchange bed exhaustion, increasing use is being made of on-line dissolved silica monitors such as the Hach 5000. However, the NRM has an advantage over the Hach monitor because it can measure both dissolved and colloidal silica. Figure 5 shows simultaneous measurements taken over a 24-hour period from both an NRM and a Hach silica monitor as an ion-exchange bed exhausts. Both instruments track the bed's exhaustion and return to near background levels as soon as the bed is replaced with newly regenerated ion-exchange resin. The slightly higher NRM readings could be an indication of the amount of colloidal silica in the water supply. It is important to remember that although the NRM can measure both dissolved and colloidal silica, it cannot distinguish between the two forms of silica.

CASE STUDY #3

Figure 6 shows the simultaneous output of a sodium analyzer and an NRM during a major power outage at a semiconductor manufacturing facility. It took almost two hours to restore power to the water system. When power was restored, the sodium analyzer showed a significant increase in sodium levels. The NRM detected the sodium as nonvolatile residue and closely followed the measurement of the sodium analyzer. Sodium and nonvolatile residue levels had still not returned to pre-power outage levels after 20 hours. It took several days to clean up to normal background levels. This case study illustrates the benefit of the NRM as a general measure of water quality, as well as verifying the NRM's performance.

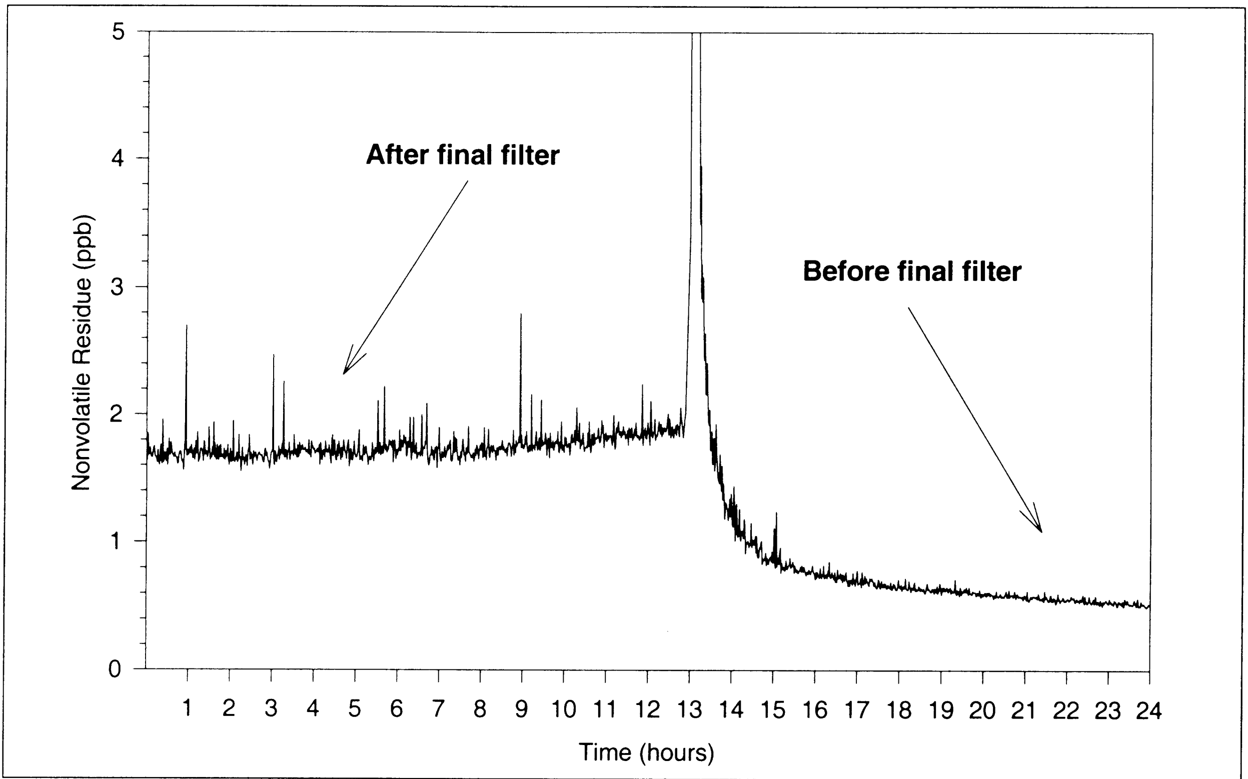

Figure 4. NRM measurements before and after a final water filter in a silicon wafer facility.

Figure 5. Simultaneous NRM data and Hach silica data as an ion-exchange bed exhausts.

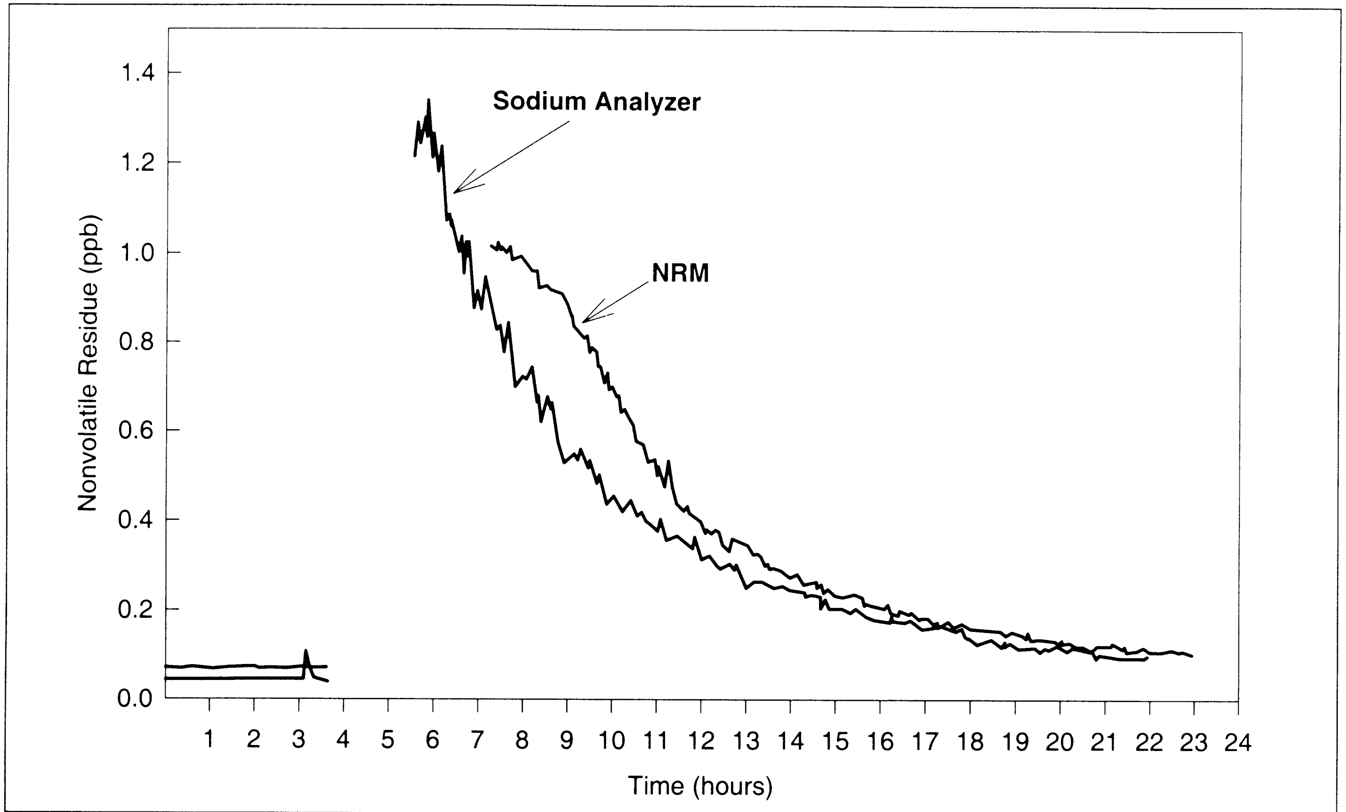

Figure 6. Sodium breakthrough measured by a sodium analyzer and an NRM.

CASE STUDY 4

The final case study measures the increase of nonvolatile residue after the water distribution pipework had been sanitized with ozone. The NRM was located at the point where water is supplied to the distribution system, upstream of the ozone generator. The residue values shown in Figure 7 were therefore measured after the ozonated water had traveled through the entire distribution system, the ozone destroying ultraviolet lights, the polishing resins, and final filters. Ozonating this particular water distribution system released a contaminant that was not completely removed after a single pass through the water polishing system. Simultaneous measurement of TOC and particles showed no corresponding increase, indicating the source of the contamination was neither TOC nor particulate in nature. The increase in nonvolatile residue was observed whenever the distribution system was ozonated.

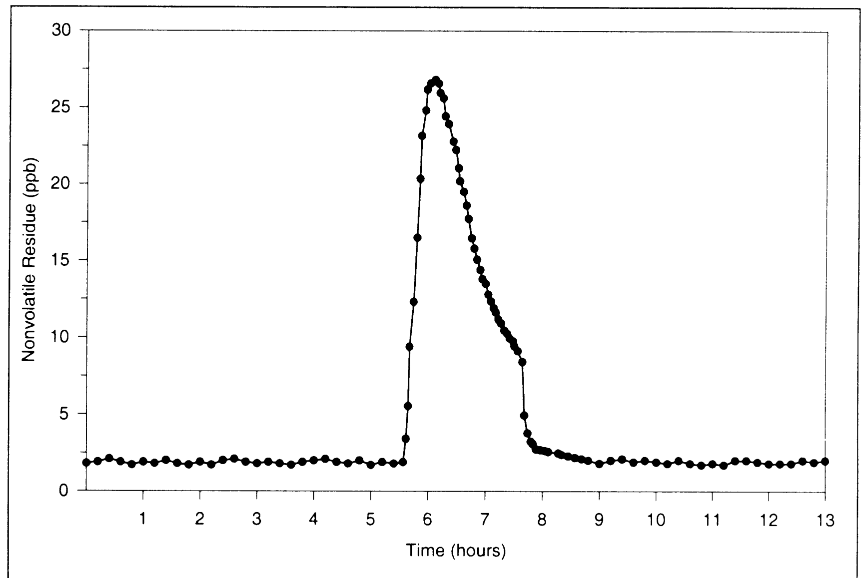

Figure 7. Nonvolatile residue measurement after ozonation.

CONCLUSIONS

The on-line measurement of nonvolatile residue provides water process engineers with an additional tool for monitoring the overall quality of high-purity water. While the NRM cannot identify individual sources of contamination, it can rapidly detect contaminants from a wide variety of sources with part per trillion sensitivity. Case studies show that the NRM can detect contamination events not currently measured by other on-line water quality monitors such as particle counters, TOC analyzers and resistivity monitors.

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