

INSTRUMENTS

SODIUM AND SILICA TRACE MEASUREMENT TO MEET SEMICONDUCTOR WATER SPECIFICATIONS

In the production of high-purity water, dissolved silica is known to be the first ion to breakthrough when the ion-exchange (IX) resin approaches depletion. Much work has been done in past decade in measuring dissolved silica online. Continuous silica monitoring after secondary mixed-bed IX in the water demineralization process ensures consistent water purity. Because of modern technologies for producing smarter and smaller devices, microchip sizes have been reduced significantly, leading to higher quality requirements for the water treatment. This trend of higher quality purified water also requires measurement of silica traces down to parts-per-trillion (ppt) level.

In the cation deionization process, it is important to monitor the resin's capacity in order to effectively retain the hardness cations (calcium, magnesium and sodium) from the water source. This article covers state-of-the-art technology to track silica levels online accurately and reliably down to 5 ppt, or 0.005 parts per billion (ppb) 24 hours a day, 7 days a week. This article also covers on-line monitoring of resin exhaustion by means of a modern sodium analyzer to identify breakthrough of unwanted ions and to signal the need for regeneration.

Reliable Sodium Measurement

A common sodium sensor shows higher sensitivities to hydrogen and silver ions than to the sodium itself (see Figure 1). Unfortunately there is no composition available that does not have the men-

tioned cross-sensitivities.

It goes without saying that (trace) sodium measurement is only possible by elimination and minimization of the hydrogen and silver ion influence. Thereby, different approaches can be seen in on-line sodium analyzers to remove those interferences and provide stable and reliable readings.

pH Control

Hydrogen ions provide the largest contribution to a sodium measurement. Lowering the hydrogen concentration means elevating the pH value of the sample. For trace sodium analysis, an alkalization of at least pH 11.5 is required to get a linear response of the sodium measurement chain down to lower ppt levels.

Ammonia in water, even at a 30% concentration is not a sufficient alkalizing reagent to shift the sample pH up to the required value. Various lab testing and field experiences have proven that diisopropylamine (DIPA) is much more appropriate and preferred in this case. Additionally, it could be seen that such high pH values cannot be reached using

diffusion tubing, so an active dosing (i.e., by an air pump) is needed, which offers much more benefits in terms of monitoring and controlling the sample pH. Monitoring of sample pH for high-purity water is very simple and can be done by conductivity measurement. With the given molar conductivity coefficient of DIPA in water and the required pH, which is a concentration as well, the required conductivity can be calculated and be used as a set point for the alkalization monitoring.

Silver Ions

Silver/silver chloride reference electrodes are the one and only source of silver ions in such a measurement system, thus installing a silver-free electrode (i.e., calomel) eliminates the problem of cross-sensitivity. Controlling and monitoring the pH/alkalization and the usage of silver-free electrodes can measure sodium without the mentioned cross-interference influence. However, to guarantee a reliable and accurate trace sodium measurement, additional measures are necessary.

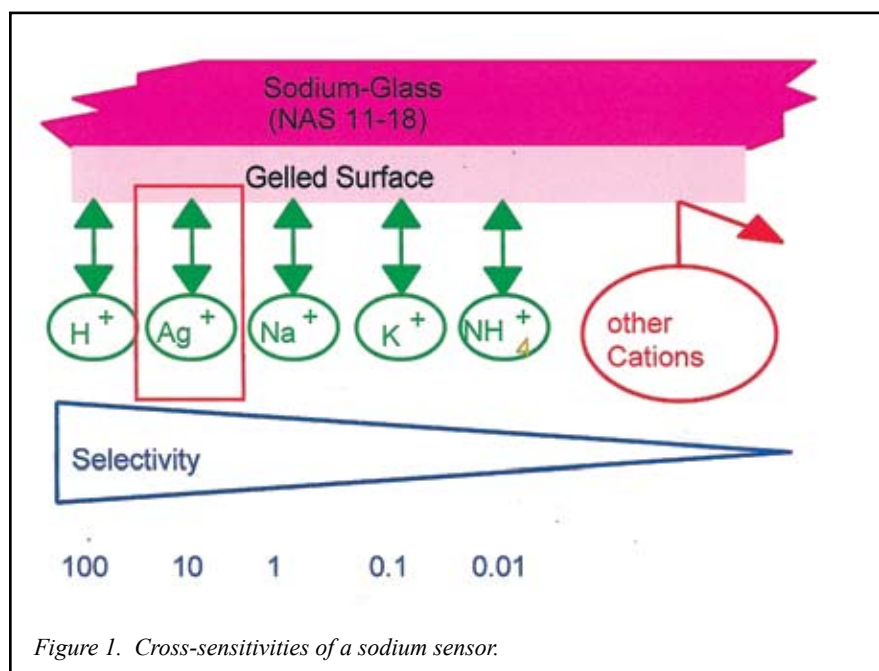


Figure 1. Cross-sensitivities of a sodium sensor.

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Calibration

Calibration is in fact a very sensitive issue because the performance of an instrument is changed. But how to calibrate an on-line trace sodium analyzer, which normally measures between 10 and 30 ppt without spoiling the performance? Unfortunately, there is no (certified) ppt-level sodium standard available. Common practice for the calibration of this kind of analyzers is a technique called “multiple known standard addition”. Three points are required to solve the unknowns— “offset”, “slope”, and “background sodium concentration”. Additionally, the third determination is used to confirm the calibration line, established by the first two measurements. It is without question that such a procedure has to be performed automatically to exclude possible errors based on manual handling.

In Figure 2, it can be seen that a low-ppb standard is required, so the question would be how to blend a stable 1-ppb standard? The secret lies in an automatic, in-line dilution (approximately 1:500) of prepared low-parts per million (ppm) sodium standard, using the alkalized, high-purity water sample in the measurement chamber. This allows the operator to prepare a ppm sodium standard that is easy to do in the lab.

An indispensable prerequisite for a successful calibration is a sodium sensor with a reasonable response time. Unfortunately, high-purity water expedites depletion of sodium in the outer layers of the sensor membrane, which results in extended response time. This in turn means that such a sensor is not suitable for a successful calibration because reaching the end value while immersed in a calibration solution takes too long (see Figure 3). The sensor needs to be treated accordingly to ensure that enough sodium is available in the outer membrane part, which results in a fast response, required for the calibration. This treatment can be either by a sodium doping, or a removal of the depleted layer (etching). Field experience has shown that only etching is an appropriate way to regenerate the sodium sensor.

Automatic calibration, including upstream automatic sensor regeneration, is the best practice for measure-

ment reliability, optimized instrument performance, and minimized manual maintenance effort.

Sample Quality Verification

In laboratory practice, the guarantee for the presence of the sample is given by manual sample collection and preparation of this sample. In an on-line system this is not the case and therefore sufficient sample availability must be monitored. In the instance of a trace sodium analyzer, flow monitoring can be done with the same conductivity probe as used for alkalization monitoring. The active dosing of DIPA always results in small conductivity changes; therefore, if no flow is present, the conductivity value remains unchanged over a certain time period, and an alarm is issued. As a second parameter for sample quality, temperature needs to be monitored as well.

Instrument Status Verification

The instruments status verification depends largely on the measuring principle. However, the integrity of the sensing system (i.e., automatic sensor etching), and the availability of all necessary resources, such as an alkalizing reagent are of paramount importance.

Trace silica measurement in ppt level.

The water used in the manufacture of high tech semiconductor and modern electronic components must be extremely pure. The specifications for every contaminant have decreased as the line width decreases. For example, at a line width of 0.18 micron (μm), the specifications for total organic carbon (TOC) and silica are 2 ppb, and 0.1 ppb, respectively. At a line width of 0.13 μm , the specs for TOC and silica are 1 ppb and 0.05 ppb, respectively.

The sooner silica can be measured; the earlier the process failure can be determined. Though most of the facilities now have water treatment that can guarantee resistivity levels of 18 megohm-cm or higher, silica can still break through at these yields.

Trace analysis techniques for ppt level on-line measurement. The actual measuring principal is reported in the ASTM D7126-10 “Standard Test Method

for On-Line Colorimetric Measurement of Silica” (1). This test method is a colorimetric method that determines molybdate-reactive silica. It is applicable to most waters, but some waters may require filtration and dilution to remove interferences from color and turbidity. This combination of using the molybdate colorimetric technique and sample concentrator can detect overall residue contamination as low as 10 ppt.

The inventor has developed the advanced technology that allows the lower limit of detection of silica by 40 to 50 times by means of a low-pressure reverse osmosis (RO) membrane. The RO module helps to facilitate the concentration of the sample silica content (sample concentrator) before analysis.

Electro-Optical Stability

A higher wavelength LED light source (815 nanometer) is employed for better stability and better accuracy for trace level and the photometry module is being heated to 45°C for faster reaction time and more stable measurement.

Principle of the sample concentrator (2). The water sample enters the RO module at high-purity water system pressure (without an additional pump). As a result, it segregates into two parts:

1. Product— pure water without any dissolved materials
2. Brine— concentrated silica from the sample

The product is partly used for the determination of the blank reading. The brine gets into the reaction chamber of the photometer module for measurement. The determination of the silica content of the sample by two steps calculation below in the next section.

Calibration

The standard calibration can be started manually or automatically. It is recommended to be done after every change of reagents. The value of the concentration should be greater than the highest value of the brine. Zero calibration is always performed automatically to check for transmitted light and to calibrate the turbidity. The product is partly used for the determination of the blank reading.

The brine gets into the reaction chamber of the photometer module for measurement. The determination of the silica content of the sample can be shown by the calculations in Equations 1 and 2:

$$\text{Concentration Factor} = \frac{\text{Efficiency} \times \text{Total Flow}}{\text{Brine Flow}} \quad \text{Eq. 1}$$

$$\text{Sample Concentration} = \frac{\text{Concentrate Reading} - \text{Product Reading}}{\text{Concentration Factor}} \quad \text{Eq. 2}$$

Field Trials

A field trial was conducted at a semiconductor 300 mm wafer fab plant. The analyzer was operational for a period of 30 days and results were promising, and the study declared successful. The comparison was done making use of ICP in their laboratory.

Conclusion

To achieve reliable and accurate trace sodium and silica measurement, different aspects have to be considered and implemented with analyzers of this nature. Chemical and physical properties have to be taken into account and eliminated or at least minimized. Adequate controlling/monitoring systems such as flow, temperature, and sample conditions are required to guarantee a proper measurement of the sample and to reduce maintenance efforts. To optimize those efforts, risk assessment of every single measurement point has to be done and the assignment of the correct quality level according to the risk. To enable a reproducible quality assurance, standard operating procedures, provided by the instrument manufacturer have to be used and followed. □

Author Morris Teo graduated from the School of Electrical and Electronic Engineering at Singapore Polytechnic in 1991. He has 20 years of operation and management experience, including domestic and international posts, from project engineer to senior manager with organizations such as Philips Electronic, Tyco, and Nova Analytics. He joined SWAN Analytical Instruments in 2007 as a regional sales manager covering East Asia and Oceania countries.

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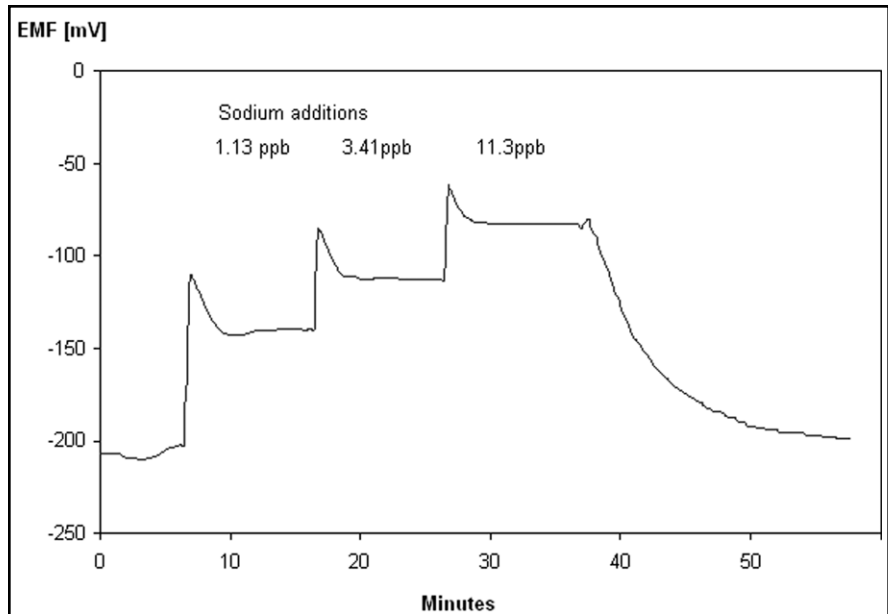


Figure 2. Three point known addition calibration of a trace sodium analyzer.

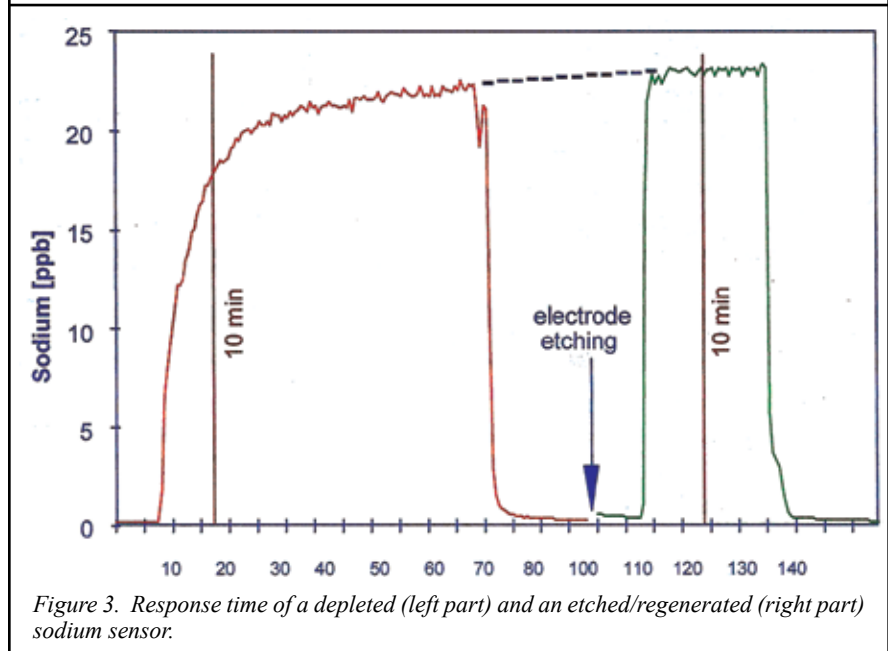


Figure 3. Response time of a depleted (left part) and an etched/regenerated (right part) sodium sensor.

1. ASTM, "Standard Test Method for On-Line Colorimetric Measurement of Silica", ASTM D7126-10, American Society for Testing and Materials International, West Conshohocken, Pa. (2010).
2. Carr, G.E. "Water Contamination Concentration Apparatus and Process", U.S. Patent No. 6,420,185 (July 16, 2002).

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Key words: INSTRUMENTS, ION EXCHANGE, MONITORING, SEMI-CONDUCTORS, SILICA