

In-Situ Chemical Monitoring in Semiconductor Fabrication Chemical Supplies

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ABSTRACT

Problem

In-coming chemical quality has been left to the chemical suppliers. Semiconductor fabricators have very limited or no capability to detect problems with process chemistries from their suppliers. This is to say that poor chemical quality is discovered through in line test data or poor e-sort performance. Chemical quality is assumed to be what has been sent from the supplier and is typically documented through a certificate of analysis. Changes than can and do occur during in-house handling are disregarded and not monitored

Historically speaking the risk from suppliers is low.

Documented mishaps for out of spec material shipments are extremely rare. In fact the semiconductor industry in general insists on suppliers with a superior quality history and a robust quality program. However, these quality programs are not perfect and there have been isolated events. Events that resulted from human error within the fabrication facility are not very well documented, but those that have been have resulted in significant losses in product, production time and in some cases process equipment damage. Once the chemical has been containerized and shipped there is very little quality control.

Factors such as human error in container handling and equipment failure at the distribution point are not accounted for.

Objective

Therefore, the product (the wafers) is exposed to any potential chemical related problems. It became obvious that there is a need to develop a method to monitor

chemical quality in-situ that will identify changes in the chemistry before it makes it to the process center. The ideal application should be easy to install, inexpensive, and easy to communicate with (for data collection and interfacing with monitored equipment). The use of custom-made equipment is also undesirable as this may limit future applications and drive up cost. It also became obvious that a single methodology was not likely going to meet the needs of the semiconductor industry. The variety and types of chemicals is too broad to consider such an answer.

Approach

It was found that product is exposed to any incoming chemical changes, no matter what the cause, supplier, mechanical or human. In fact it can be said that the product is used as a monitoring method for the chemicals. Detection of these changes is limited and in some cases unreliable. In most cases this means that some portion of the product has been exposed to the out of spec material that would in turn cause rework or scrap. Detection capabilities and sensitivities are also further reduced by ever decreasing in-line testing driven by the CFM processing methodology and other time to market pressures facing all types of fabrication and manufacturing operations.

Status/Summary of Findings

This paper will discuss a variety of different monitoring methodologies; suggest the best practices for a cost efficient application for a wide variety of semiconductor chemistries. The solution to the overall problem is not a single device or scheme, but rather a set of devices and a change to fundamental thinking in the chemical distribution area. Supporting data and other relevant

experimental results will also be discussed to support and reinforce the findings.

INTRODUCTION

Background

Philips Semiconductors (now NXP) in Fishkill, New York had a series of chemical supply related issues in their WETS processing center. Investigations of each event were followed with corrective actions. Each event generated a specific action geared at correcting and/or preventing a reoccurrence of that specific event. The Failure Modes and Effects Analysis (FMEA) system was implemented throughout the Fab. Based on the FMEA methodology some deficiencies were clearly identified. The deficiency that stood out the most was the lack of detection and the lack of the ability to prevent such a failure from re-occurring. In-line measurements and equipment checks such as etch rate monitors or particle counts were depended upon to identify a problem. By the time the problem reached this level there was already product and equipment that had been exposed and potentially damaged or scrapped. In addition the International Sematech Manufacturing Initiative has published data that show that the chemical supply is one of the top five facilities related reliability issues for ten years running. Thus making chemical distribution related improvements imperative.

Objective

The objective of the work and this paper is to identify the chemical monitoring techniques that can be employed in situ for chemical supply systems. This addresses the need for improvement of the detection of problems before they reach the manufacturing area. The refractive index technique is discussed as the most cost effective and reliable method to monitor a wide variety of chemistries. This paper will not discuss the actual techniques in any great detail. There are a large variety of

resources available to research this matter and is not the intention or the goal of the work performed in writing this paper. Instead the application is discussed in terms of establishing a method to detect potential problems and protecting the fabrication of quality products. Issues with regard to implementing the techniques are addressed. This monitoring technique coupled with a robust drum tracking system can protect the equipment, product and most importantly the people from failure. The combined applications will increase the detect ability of an event to near 100%.

Methodology

The selected method must be cost effective, low maintenance, robust in terms of “false alarms”, and easy to integrate into the equipment. Integration, in this case, pertains to communicating with the distribution equipment and data collection capability.

Special attention was given to finding a method or methods that would lend themselves to a combination of many attributes. Reliability, maintainability, cost, cost of ownership, ease of integration are all critical attributes.

Compatibility with semiconductor grade chemicals was also an important consideration. The device(s) selected could not be a cause of or contribute to trace metallic or particulate contamination in order to be considered.

General

All methods of chemical monitoring were considered. Various forms of physical properties of chemicals were considered. Instruments to measure electrical properties are readily available but can “drift” with time and require frequent maintenance. Electrical properties are also easily fooled even if the chemistry has in fact changed. There are many chemistries with similar electrical properties making detection of a mixture, in this application, undependable. Temperature compensation in

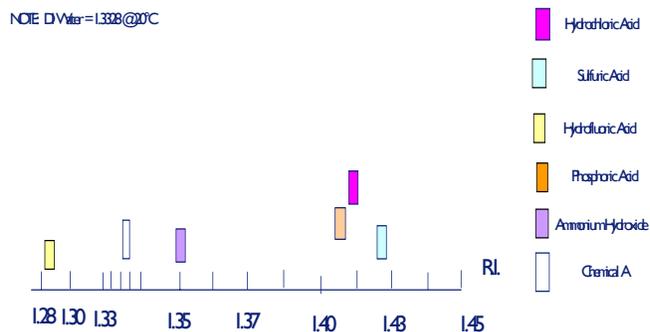
these instruments is often not very good and adds to the potential for error, including the drift previously mentioned. Instruments that are used cannot be prone to false alarms, which we could see with this type of measurement.

Cost and ease of integration, two other required features also eliminated measurement options such as autotitration. Autotitration is expensive and requires frequent maintenance. Integration into some equipment would be difficult as well. This is especially true if one titrator is used to monitor many chemical delivery systems. If one autotitration system was used to monitor many distribution systems, that would leave equipment unmonitored for periods of time while it was scanning through the other systems. Depending on the number of systems and the types of titrations being performed the unmonitored times could be lengthy.

The pH is also a property that is easily fooled even if the chemical make-up changes. The probes are also an issue in this type of service. They require frequent maintenance and there are some compatibility concerns, especially with fluorides or chemicals that contain fluorides.

The refractive index of a chemical on the other hand is known and it is very rare that two chemicals have the same refractive index. Figure 1 shows a graphic display of the refractive index of many typical semiconductor chemicals. The chart should be completed with the refractive index range for each chemistry. This chart should be completed for the chemistries that you have to show what risks there may be due to chemicals' refractive index over lapping. This completed chart, along with the layout of the locations of the similar chemicals are required in order to determine how to set up this technique in the fabrication facility.

Figure 1 Refractive Index of Some Common Semiconductor Chemicals



The refractive index will change for a known concentration of a material two ways. [1] The first is by changing the wavelength of the light source. The second is by changing the temperature of the media to be measured.

Refractometers have a constant light source, usually an LED. Most published data is given at 20° C or 25° C. However, in application the temperature was found to be between 21° C and 22° C. Formula 1 can be used to predict the change in refractive index based on temperature for most¹ chemicals. Figure 2 shows the change in refractive index based on the change in temperature. Hydrogen Peroxide, in a closed system, was heated by 2° C and the temperature compensation was disabled. The 2° C shift in temperature translated into a .27% weight change in assay. The change in terms of refractive index is .0012. This correlates to ~.1% weight change in assay for each degree Celsius change. The change in assay with the temperature compensation turned on was negligible, as expected. Refractive index is a physical property that is dependent on the temperature of the liquid that is being tested. Literature values for refractive index, however, will only be given for one particular temperature (usually 20° Celsius). For this reason, it is necessary to be able to manipulate the experimental values of refractive index so that they can be compared to the values found in literature.

Knowing this relationship, and the temperature at which the refractive index was experimentally determined, the experimental value can be transformed in such a way that it can be properly compared to the literature value.

Formula 1

$$n^{20} = n^t + .0004(T - 20) \quad [2]$$

Table 1 Calculated RI based on Temperature Changes

Chemistry	Published RI	Reference Temp	RI calculated for Delta T	Measured RI
Sulfuric Acid	1.427	21	1.4254	1.4257
IPA	1.3796	15	1.3764	1.3761
HCl	1.4184	20	1.4204	1.4171
H2O2	1.3526	20	1.3532	1.3534
H3PO4	1.4368	20	1.4388	1.4318
NH4OH	1.336	20	1.338	1.3469
HF	1.2867	20	1.2887	1.2858
NMP	1.472	25	1.4710	1.4698
PGMEA	1.401	20	1.4020	1.4009
EKC 265	1.4474	20	1.4484	1.4485

Sudden changes in material temperature outside of a few tenths of a degree Celsius are uncommon in chemical distribution supplies. A two-degree shift would be considered huge in this application and the resulting assay shift is negligible for most of the chemicals, as this would represent a 10% change versus the acceptable range which is generally 2–2.5% range.

Figure 2 Change in refractive index due to change in temperature, un-compensated.

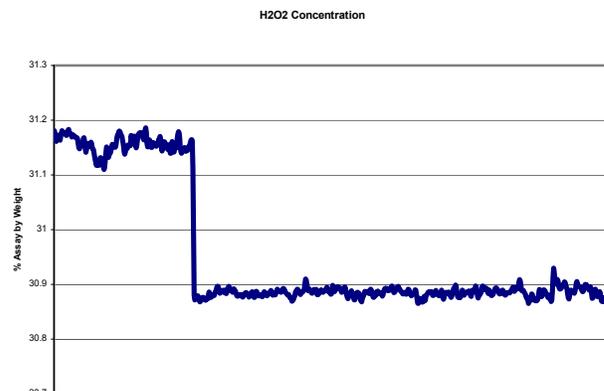
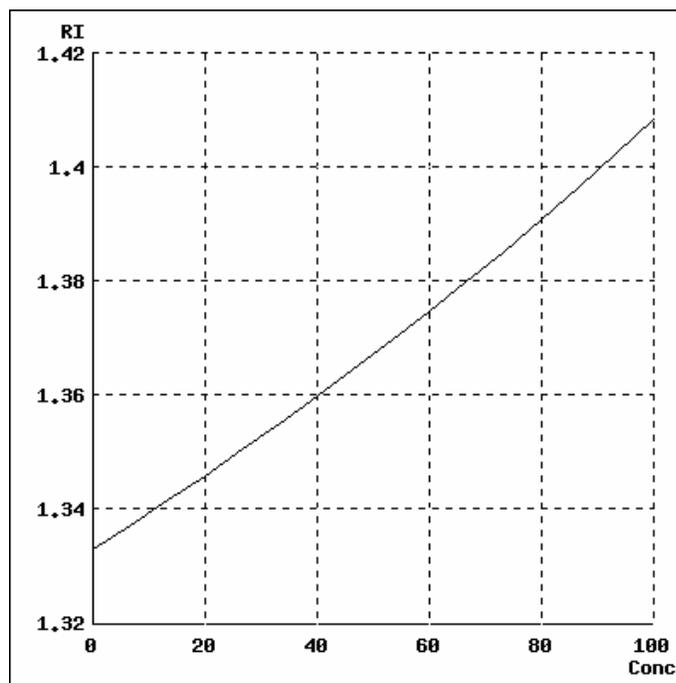


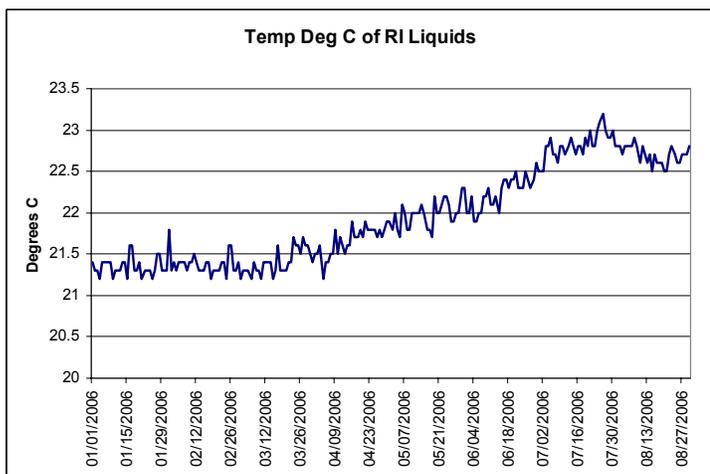
Figure 3 Hydrogen Peroxide RI vs Concentration (weight %)[4]



The refractive index of most chemicals is linear at a constant temperature. This is the ideal case for chemical distribution systems that typically are at a fairly constant temperature and only prone to seasonal fluctuations. Figure 4 is a chart of the temperatures that we saw over the course of 8 months. Prior to

implementing this technique in any facility this parameter should be measured so the temperature fluctuation is understood. The two major areas to consider are the chemical deliveries and environmental controls of the distribution space. Chemicals are typically stored in an off-site warehouse and delivered to the Fab for use as required. The only concern would be if the chemicals were in transit for an extended period of time in an uncontrolled or poorly controlled environment. Material temperature tends to fluctuate with the seasons (North Eastern U.S.)

Figure 4 Eight Month Temperature Trend



The temperature compensation in the refractive index meter is robust. In addition the effect of the temperature fluctuations that were typically seen on the refractive index were not as drastic as on other types of measurements and therefore not as critical. Refractive index is not sensitive to changes in pressure or velocity. Measurements can be buffered to reduce, and in most cases eliminate, the effects of bubbling or foaming.

All of these facts greatly reduce the possibility of generating a false alarm. Within the first week of their initial installation the refractometers alarmed three times. Each event was confirmed to be genuine with a sample that was titrated. In all three cases the titrated sample was

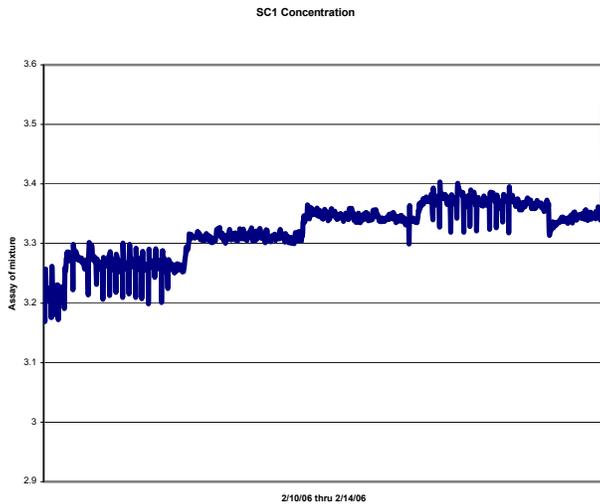
within .2% assay of the refractometer read out for the event. Table 2 below shows these results.

Table 2

Chemistry	Refractometer Assay	Titrated Assay
Ammonium Hydroxide	29.5%	29.4%
Hydrofluoric Acid	48.8%	49.1%
Ammonium Hydroxide	29.5%	29.3%

Monitoring of custom dilutions is also possible with this technique. The major difference being that all of the refractive index ranges and set points have to be done locally by experiment. Figure 5 is a custom blend from the Philips Fishkill Fab. The components are Ammonium Hydroxide, Hydrogen Peroxide and De-ionized water that is a common blend to most semiconductor manufacturers. However, the ratio for this blend is different for each fab and some fabs use many different dilutions. Figure 4 is data that was taken from an older blending system. The trend shows that the blend is gradually getting stronger. This data was confirmed through lab analysis. It was determined that the day tank of this material would slowly weaken and that the addition of the fresh blends gradually strengthened the contents. The day tank has been removed and the chemical is blended on demand. The process yield that this chemical is used for has improved as a result of this change.

Figure 5 Custom Chemical Dilution Monitoring



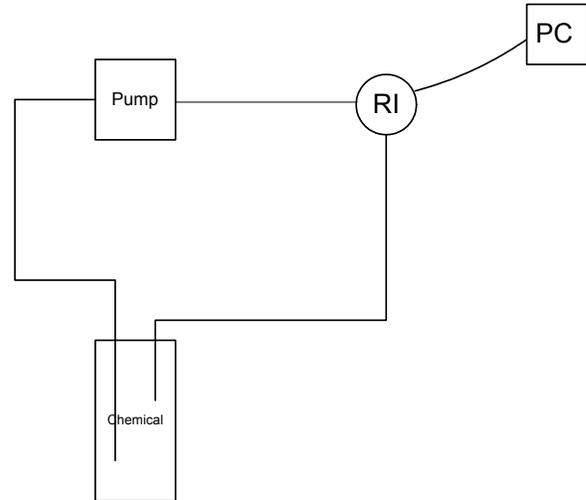
It was found that refractive index was not effective on monitoring the content of a surfactant in a solution. Typically surfactant dosing is measured in part per million (ppm).

The two instruments that were used both came calibrated from the factory and ready for use. However, they also both offer the capability to “dial in” the instrument to a specific application. In the case of chemical distribution this is a desirable feature. The instrument can be calibrated to focus on a particular portion of the refractive index curve for a given material. Conversion to weight percent assay is a standard feature but should not be used in all cases. Establishing an acceptable range of refractive index is equally effective. We found this to be especially handy on any custom blend chemicals where some of the components maybe proprietary.

The most effective method to field calibrate the instrument is on the bench top. The schematic in Figure 6 shows the plumbing requirements. The container holds a known quantity of a known concentration to which a known amount of impurities are added. This method is extremely effective for calibrations of an existing process.

The process window can be defined in terms of refractive index and alarm set points set up accordingly.

Figure 6 Refractometer arrangement to collect data

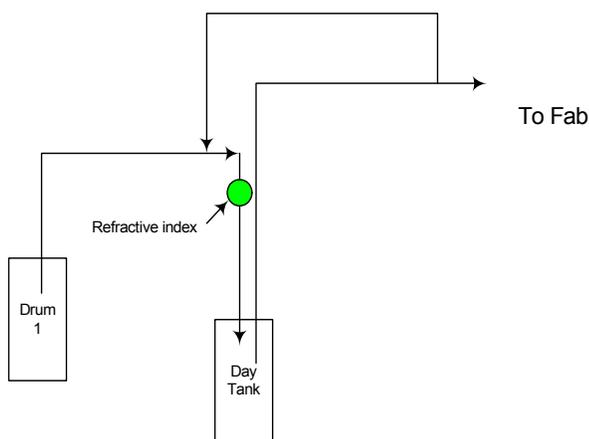


Once the device is installed recalibration can be done using two different techniques. The first is to repeat the installation process, but this would mean removing the device from the distribution tool. Removal is required because you would want to contaminate the distribution system with the calibration chemical. The second is to use Deionized water (DI Water) of which the refractive index is known to be 1.3328 @ 20°C. As long as the chemical that is being monitored has not changed this method is very efficient. In most cases the instrument does not have to be removed since most distribution tools have DI water and high purity Nitrogen (HP N2) for maintenance purposes. Run the maintenance program for the section of the tool that contains the refractometer and record the refractive index.

Positioning the refractometer is critical in protecting the processes. The ideal location will allow for the monitoring of chemical into the fab as well as drum changes. This can be difficult or impossible depending on what brand and model chemical distribution system you are using. The features that are on the system may also effect your installation.

PSF uses BOC Edwards's model 1515 and 1535 distribution systems. The difference between the two is the type of distribution engine employed. Note in figure 7 the installation of the refractive index. We are able to monitor new chemical being loaded as well as chemical being sent to the fab and the chemical as it is polished.

Figure 7 Refractometer placement.



The refractometer signals are wired into one of the on-board, inputs. We use the “remote EMO” signal which was previously unused in our tools. It is important that all of your systems are connected in the same manner so that maintenance personnel know the problem as soon as they see that alarm message.

Shutdown set points are determined by the incoming chemical quality. Set points for the shutdown are set within the acceptable limits of the chemical. For example if the range of assay for Sulfuric acid is 95% to 98% the limits for the refractive index system maybe 95.5% to 97.5 %. Therefore the processes are truly protected from the material going out of specification. Shutdown of the distribution system occurs as the limit is approached, not violated, very similar to a statistical process control program would do.

The only chemical parameter that was not detectable via refractive index was surfactant concentration. Typical surfactant concentrations for buffered hydrofluoric acids and developers are only few

part per million (ppm). Results of testing with refractive index were unreliable and not repeatable. This is to say that the refractive index response to surfactant changes was inconsistent. The only testing that was found to detect these changes is dynamic surface tension. The dynamic surface tension mimics the standard lab test for this same parameter, which is the static surface tension. The difference being that the dynamic surface tension is the surface tension of the solution as it is moving, which is more like the actual process condition.

The dynamic surface tension test, however does violate one of our primary guidelines with regard to integrating into the tools. It is difficult to integrate and be difficult to set up as an in-situ test.

CONCLUSIONS.

Monitoring facilities services in semiconductor fabrication plants is imperative. In fact many facilities services are and have been monitored for a long time. However the chemical supplies have, for some reason, fallen behind that curve. As we have seen there have been events that indicate that considerations must be made to change this situation. There is published data that also re-enforces the need and finally there is the FMEA review. Some sort of chemical monitoring must be utilized along with other safeguards to reduce the possibility of human error and improve detection of other changes.

It has been shown that implementation of these changes is economically feasible (less than the cost of the labor to correct a major event). It should also be noted that expertise in the chemical distribution area should not be overlooked or under estimated. Instead this should be treated as a critical tool set capable of causing significant impacts to a fab very quickly.

The instrument(s) selected were applied to previous events to determine their effectiveness in application. That is the data from previous events was used to create the changes in chemistry and the resulting refractive index was measured. It was shown for each

case that these devices did in fact respond to the incidents and would have detected them had they been in place.

The first three refractive index devices were installed in December of 2004. They were all qualified and released for full function in January of 2005. Within a few days we had our first shutdown. The refractive index of HF 49% was measured to be 48.5%. Lab data for the sample taken at the time of the event was 48.4%. There were two other shutdowns shortly there after. We have concluded that this is normal drum-to-drum variation. A random sample of 10 drums of HF49% was taken when they arrived in our warehouse. All 10 drums are from the same manufacturers lot. Table 3 shows the results. Similar results were seen and confirmed with ammonium hydroxide 30%. A random sample of 10 drums was also taken on incoming drums of ammonium hydroxide. The results are in Table 4. There are currently studies going on to see if there is any effect on any of the processes that use these chemicals. Process yield and e-sort yields can be vintaged to the tools that had these chemicals in them. These drum-to-drum variations were probably always there, they had just never been measured before.

Table 3 HF 49% Drum samples [3]

<i>Drum #</i>	<i>Assay</i>	<i>Incoming Assay</i>
1	49.1	49.2
2	49.2	49.2
3	48.8	49.2
4	49.1	49.2
5	49.2	49.2
6	49.2	49.2
7	49.3	49.2
8	49.1	49.2
9	49.1	49.2
10	49.0	49.2

Table 4 Ammonium Hydroxide Drum samples [3]

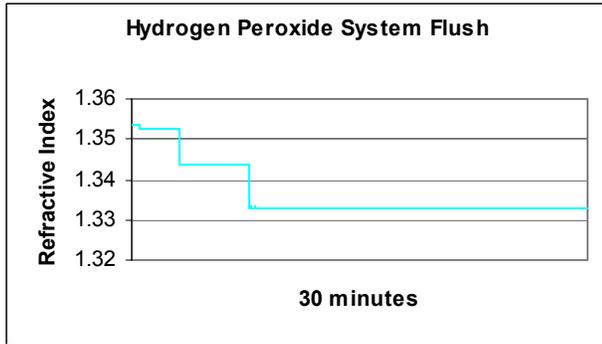
<i>Drum #</i>	<i>Assay</i>	<i>Incoming Assay</i>
1	29.6	29.9
2	29.7	29.9
3	29.7	29.9
4	29.9	29.9
5	29.8	29.9
6	29.8	29.9
7	29.7	29.9
8	29.8	29.9
9	28.8	29.9
10	29.7	29.9

The instruments have been networked and the actual data is logged and charted in an SPC type application. Any drifts or trends can be quickly identified and addressed before they become an incident to the manufacturing operation.

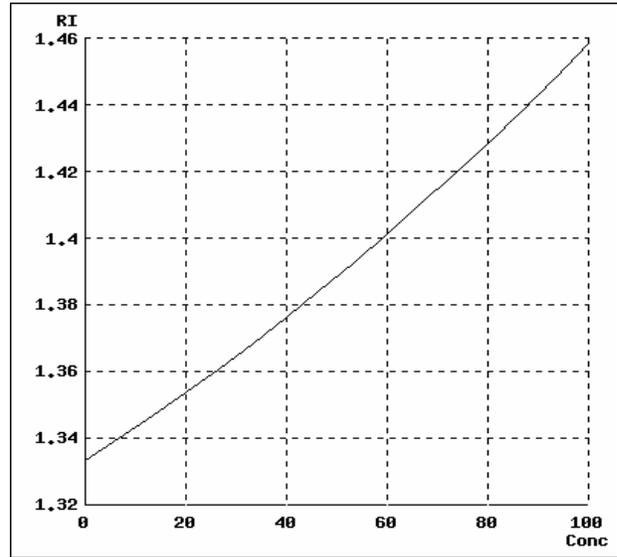
A standard operating procedure (SOP) should be developed instructing chemical operations personnel how to respond to an alarm. This will vary for each fab and there may be a need for different responses for different chemistries. A matrix is a very effective tool to communicate the this type of information.

The refractive index devices are reliable and do not require a lot of maintenance. We have been able to incorporate the calibration check into our regular annual maintenance activities. The DI water flush time is extended to ~10 minutes and the refractive index is measured for the duration. The graph in figure 8 shows a typical curve as the chemical residue is purged and the system cleans up. This chart is for 30 minutes and is typical of other results. These are typical pre-maintenance purge sequence values. This type of work is done during routine annual preventative maintenance when the tool is down to manufacturing. This step adds 10-12 minutes to the PM. Maintenance is easy and does not require a lot of experience or expertise with the instrument.

Figure 8 Sys tem Flush with DI Water



Phosphoric Acid Refractive index



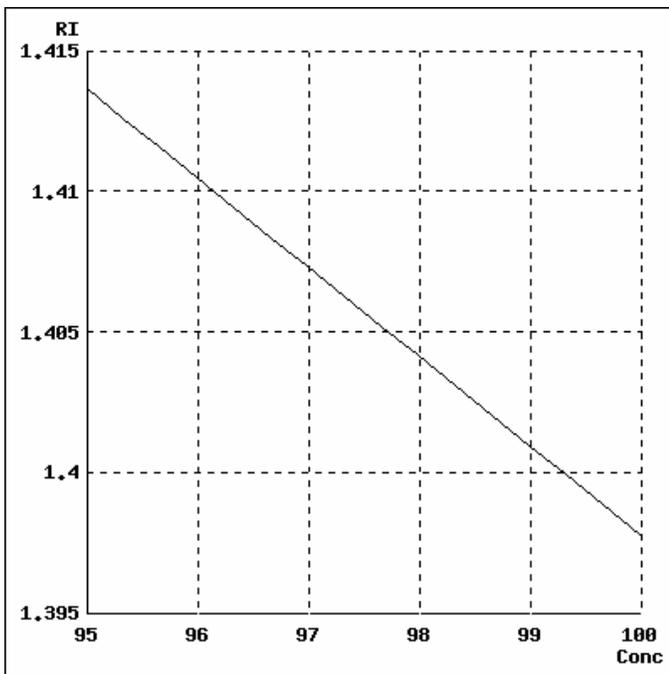
APPENDIX A – REFERENCES

- [1] Chemical Technicians Ready Reference Handbook, 3rd Edition. McGraw Hill; 1990
- [2] wulfenite.fandm.edu/labtech/refraction.htm
- [3] assay by titration Balazs Labs, Dallas, Tx.
- [4] www.kpatents.com

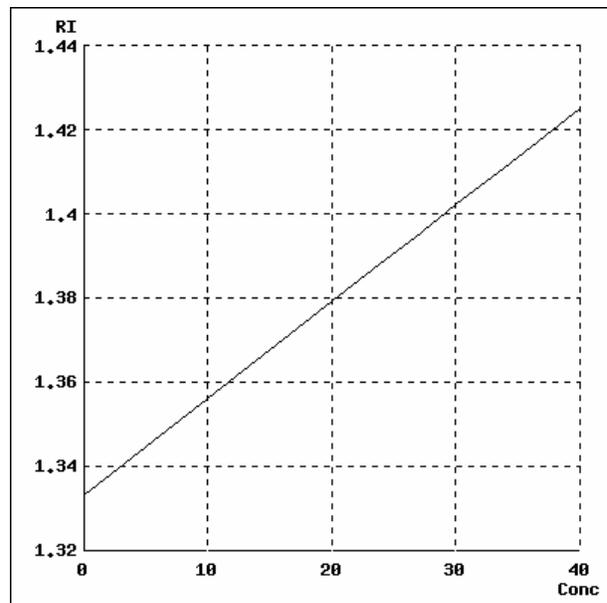
APPENDIX B REFRACTIVE INDEX REFERENCE CHARTS

Source: www.kpatents.com

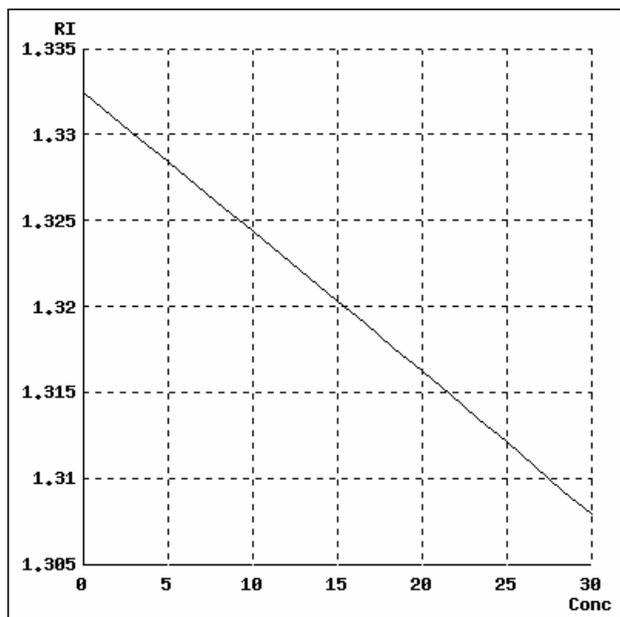
Sulfuric Acid Refractive Index



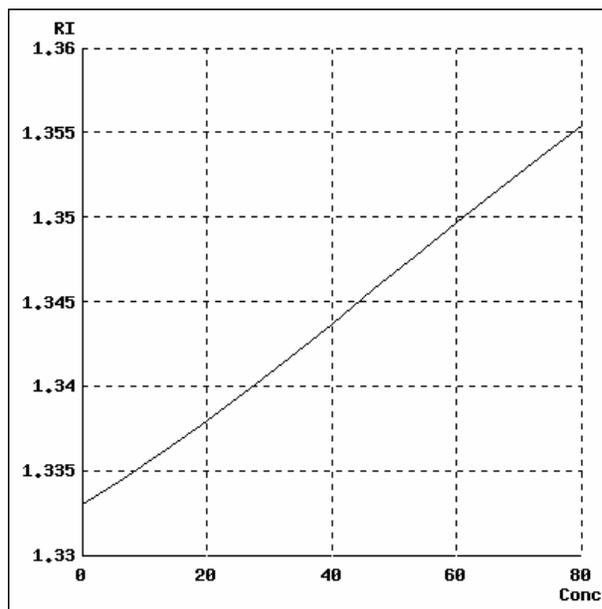
HCl Refractive Index



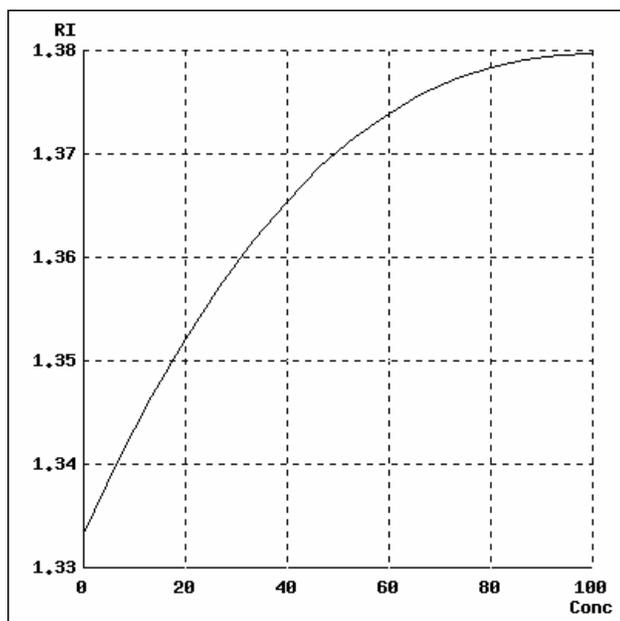
HF Refractive index



NH4OH Refractive Index



IPA Refractive Index



Nitric Acid RI versus Assay in Weight %

