Concentration Monitoring & Closed Loop Control – Phase 2

Umut Tosun, M.S.Chem.Eng., ZESTRON America
Axel Vargas, ZESTRON America
Manassas, VA
Bryan Kim, Ph.D, Pressure Products
Charleston, WV

Abstract
Historically, the determination of the concentration of cleaning agent in high precision electronic cleaning baths has depended on any one of several possible measurable parameters. Refractive Index (RI) is by far the most common. RI methods are excellent tools for use in simple systems where a single solute dominates the signal. In these situations, it is possible to characterize and calibrate how that solute affects the signal. However, the introduction of flux residues during the wash bath lifetime complicates the bath chemistry/physics to such an extent that RI signals no longer provide the same insight.

The introduction of flux residue has an enormous influence on the Refractive Index. Alternative means of measuring cleaning agent are necessary if cleaning agent concentration is to be known throughout the life of the bath. With a means to accurately measure bath cleaning agent, closed loop automated process control on the cleaning bath is possible; automating this labor intensive step in the production of electronic boards. We have found that acoustic measurements of cleaning bath solution are relatively independent of pH, conductivity, and dissolved solids in some of the most flux loaded baths. Utilizing acoustic sensing technology, field data was gathered from two beta site locations assessing the accuracy of the technology in fresh as well as contaminated wash baths.

Introduction
Aqueous based cleaning systems utilizing custom engineered cleaning agents have become the standard within the electronics industry to effectively clean electronic assemblies. For spray-in-air systems, typical wash bath concentration is maintained in the range of 10% to 20% by volume. Critical to the efficiency of these systems is wash bath concentration monitoring and control. However, as the electronic assemblies are cleaned, contamination, mainly comprised of solubilized flux residues, accumulate in the wash bath. Additionally, during the normal course of operation, wash bath volume is reduced due to evaporation and drag-out, thereby further affecting its concentration. Left unchecked, the effectiveness of the cleaning system is compromised and the expected cleaning results will not be achieved.

There are numerous wash bath concentration monitoring technologies available, however, each has its advantages and disadvantages. At SMTAI 2013, a technical study titled **'CONCENTRATION MONITORING & CLOSED LOOP CONTROL – A TECHNOLOGICAL ADVANCEMENT'** [1] was presented detailing the available technologies. Additionally, the latest concentration monitoring technique was presented, that is, one that employed acoustic sensing technology (referred to as Flowsensor). A comprehensive Design of Experiment (DOE) was executed whereby current concentration monitoring methods were examined and compared with that of the Flowsensor technology.

The SMTAI 2013 study was limited to RMA flux residue and a single micro phase cleaning agent. Comparative test data was presented as well as preliminary field data from one beta site. The results of this study verified the accuracy of acoustic sensing technology for concentration control in the presence of flux residue.

In this study, extensive Flowsensor field data is evaluated that was generated from two locations, herein referred to as Beta Site A & B. At Beta Site A, the original beta site reference in the 2013 SMTAI study, the Flowsensor technology is employed for concentration indication only. In this case, the process included an RMA flux system and micro phase technology cleaning agent. Wash bath make up or the addition of DI-water and concentrate, was manually completed based on the Flowsensor concentration readings.

At Beta Site B, the Flowsensor Closed Loop Control System (Flowsensor CLC) was employed in a closed loop control system whereby DI-water and concentrate make-up is automatic, thereby maintaining the wash bath concentration at the desired level. In this case, the process included both RMA and water soluble flux systems and dynamic surfactant cleaning agent technology. In both cases, the Flowsensor concentration reading was verified by generally accepted alternative techniques.

Accurate concentration measurement in the presence of contamination is necessary for any concentration measurement technology. For this study, the authors decided to use Non Volatile Residue (NVR) analysis as a contamination measurement [2]. Utilizing the wash bath samples obtained from Beta Site B, NVR analyses were conducted and referenced as an indicator of contamination load as well as the accuracy of the Flowsensor CLC system to indicate and control wash bath concentration in the presence of contamination.

The background information presented within this study is taken from the original SMTAI 2013 paper. The pros and cons of initial concentration analysis techniques are presented, as well as the results of the initial DOE detailing the preliminary evaluation of acoustic sensing technology for engineered cleaning agents.

Background
(Excerpt from 'CONCENTRATION MONITORING & CLOSED LOOP CONTROL – A TECHNOLOGICAL ADVANCEMENT' [1]):
Use of Refractive Index is a reliable method to determine fresh cleaning bath concentration. Refractive Index of a medium is a measure of the speed and direction of light passing through the medium and this is ideal for a pure solution (Figure 1). For a fresh cleaning agent, there is a linear relationship between the Refractive Index value and the cleaning agent concentration. A refractometer is an inexpensive, fast, and easy-to-use instrument that measures the Refractive Index. However, in the world of aqueous cleaning, wash baths become contaminated with flux residues over time. Flux residues affect the speed and direction of light as it passes through the sample medium, thereby introducing unpredictable measurement errors [3].

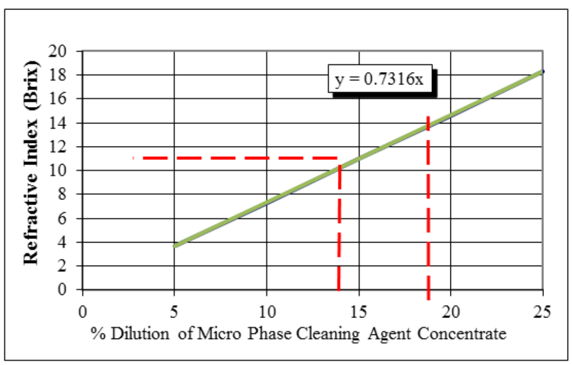

Figure 1 – Refractive Index Fresh Cleaning Agent

This measurement error, typically an overstatement of concentration, will lead to the wash bath being diluted with DI-water, further diluting the overall wash bath concentration. Thus, the cleaning process operator will believe the process is in control when in reality, it is not and likely the electronic assemblies processed are outside the cleaning specification. Flux residues remaining on the electronic assemblies can lead to field failures such as leakage current and dendritic growth.

Thus, there has been a drive to develop more reliable concentration measurement techniques.

For cleaning agent manufacturers that develop and blend their solutions, Gas Chromatography (GC) is an ideal test method for fresh or an uncontaminated wash bath. In this case, all constituents are known to the manufacturer and can be easily identified. When trying to examine contaminated samples with unknown constituents, having to select appropriate columns ahead of the analysis is difficult at best. Complications arising from the presence of unknown components are common to virtually all chemical analysis techniques, including chromatography. Thus, it is necessary to rely upon experienced analysts making sensible accommodations for the presence of unknown species based upon the fact that major contaminants can be reasonably estimated using flux formulations. It is also necessary to refrain from expecting the same quantitative accuracy as in uncontaminated samples. With such caveats, GC remains a useful, yet non-practical technique for analyzing contaminated samples.

The chemical situation is further complicated in a mathematical sense by the fact that the total number and type of species within a contaminated wash bath is unknown. Thus, in such a multi species environment, the practical approach to characterization is to choose sensing techniques based on their selectivity; that is, one chooses a sensing technique that returns a large signal for the species of interest, and a small or no signal for other species.

Trying to bridge the gap between the inaccuracy of Refractive Index measurements when used for contaminated wash baths and the inherent difficulty of analyzing unknown and non-volatile species through the use of GC, has fueled the drive to develop alternate technologies. One approach to maximizing selectivity is to target the chemical behavior of the known components of the cleaning agent. This approach enables the chemists who develop the cleaning agents to choose from a very large universe of possible chemical behaviors and reactions to precisely target the desired species. Therefore, the next step in the evolution of concentration measurement tools was the development of the chemically targeted phase separation analysis technique.

One such commercially available technique is the ZESTRON® Bath Analyzer. The Bath Analyzer was designed as a targeted reaction for the selected cleaning agents. During the development and beta testing of this product, the results obtained using this technique were compared directly against those obtained through GC analysis for both a fresh cleaning agent (Figure 2) as well as a flux contaminated bath at a customer location (Figure 3). In each case, a micro phase cleaning agent was analyzed.

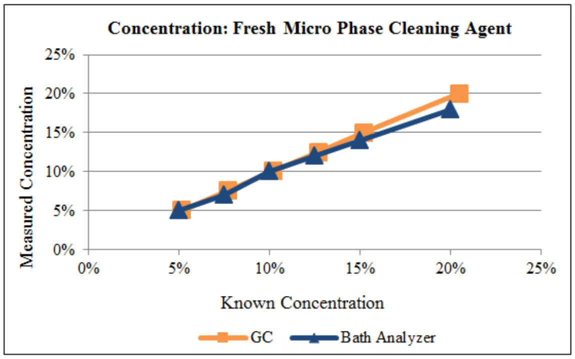

Figure 2: GC & Bath Analyzer test data – known concentration

As can be seen in Figure 2, the concentration measurement results using the GC and Bath Analyzer techniques accurately indicate concentration when compared directly against the known concentration of fresh aqueous engineered cleaning agent.

Figure 3 represents GC and Bath Analyzer data from a customer location. This data was developed through the analysis of partially loaded bath samples collected from a batch cleaning application over a four week period. As noted in the graph, the concentration as measured by the Bath Analyzer technique closely mirrored that of the GC analysis with a maximum difference of 3%.

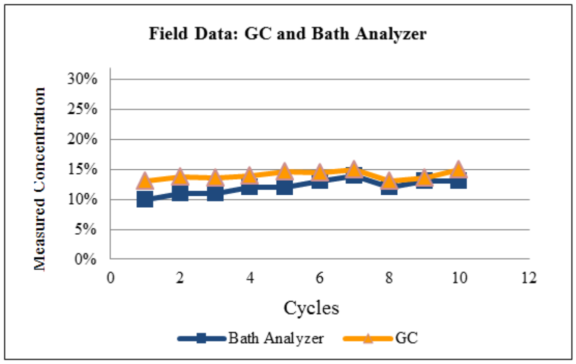

Figure 3. Field Data: GC and Bath Analyzer

The development of the Bath Analyzer for concentration measurement was a pivotal advancement. With the use of this technology, a line operator has the ability to accurately analyze a wash bath sample in real time. On the basis of this analysis, the operator could add concentrate or DI-water as required in order to maintain the desired wash bath concentration. Additionally, when analyzing alkaline products, a color reaction indicates if the alkalinity of the wash solution is satisfactory, and that is an indication of wash bath life. The Bath Analyzer technique is a manual process whereby the operator must extract a well-mixed wash sample, typically from the spray bar, monitor the process daily, and add concentrate and/or DI-water as required.

Figure 4 represents data from a customer that was using an inline aqueous cleaner and micro phase cleaning agent. In this case, there was a wide concentration process window of control ranging from 12.5% to 20% with an average of 16.25%. The process was monitored over the course of several weeks by both Refractive Index and Bath Analyzer and the concentration was manually corrected as required. As can be seen in the graph, it is clearly evident when the concentration drifted and when corrective action was taken, that is, concentrate was added to bring the wash solution back into the targeted concentration range. Throughout the testing period, the concentration determined by the Refractive Index continued to be overstated reaching a maximum reading of nearly 38%. Had the operator reacted to this erroneous reading by adding DI-water, the wash bath concentration would have been significantly diluted, inhibiting cleaning effectiveness and potentially impacting the reliability of the electronic assemblies.

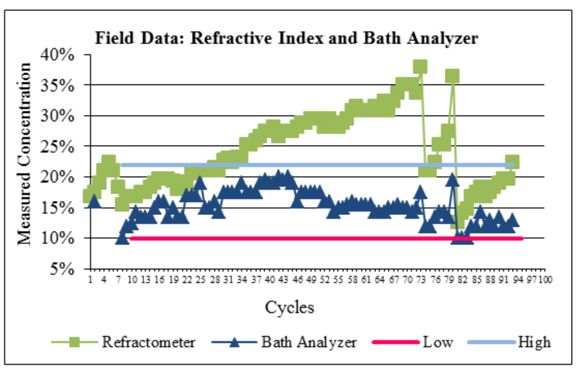

Figure 4. Field Data: Refractive Index and Bath Analyzer

Since 2009, the Bath Analyzer technique has become the recommended alternative to refractometry for fast and accurate wash bath concentration measurement. However, the desire remained to develop an inline method that could indicate accurate wash bath concentration automatically, consistently and in real time.

The authors determined that the solution for assessing wash bath concentration resided in measuring liquid flow concentration 'in line' as the wash solution is pumped to the spray bars, for this is the liquid that is in direct contact with the assembly surface during the cleaning process. Careful consideration was given to numerous available sensor options including capacitance, acoustic and optical. However, identifying a technology and adapting it such that its output can be calibrated for an aqueous based cleaning agent in the presence of flux residues as well as other process contaminants posed a significant challenge.

As noted earlier, fresh wash bath concentration is an engineered aqueous based cleaning agent and thus all constituents and their relative proportions are known to the manufacturer. Given this fact, numerous concentration measurement technologies were considered by the authors and ultimately an acoustic method was chosen as most appropriate for this application. Primarily, this decision was made due to its selectivity toward the desired cleaning agents under consideration. Initial testing of the acoustic sensing technology was limited to mildly activated rosin flux or RMA and a micro phase cleaning agent.

The selected concentration measuring device, herein labeled as Flowsensor, included an inline flow sensor and digital controller for concentration and temperature display. Ultimately, two Flowsensor types were evaluated; a handheld benchtop device for single point measurement as well as an inline device for continuous inline measurements. Both Flowsensors capture not only acoustic wave data, but also the signal amplitude and signal dampening effect over time. The results of each were found to be nearly identical.

This concentration monitoring technique was evaluated using a micro phase cleaning agent. Details are as follows:

- Cleaning Agent Concentration Analysis (Figure 5):
    - Fresh wash bath at a known concentration is analyzed and results compared with the Flowsensor (handheld), GC and Bath Analyzer
- RMA Flux Load Analysis (Figure 6)
    - Flux loaded (1%) wash bath is analyzed and the results compared with the Flowsensor (inline), Bath Analyzer and Refractive Index

All tests and data analysis were performed at the ZESTRON Technical Center.

Cleaning Agent Concentration Analysis (micro phase cleaning agent)
Figure 5 represents the GC, Bath Analyzer and Flowsensor data as compared to the known cleaning agent concentration. For Flowsensor measurements, the cleaning agent temperature was 60°C whereas for Refractometry and Bath Analyzer, measurements were taken at room temperature. For GC analysis, the standard temperature protocol was followed.

As indicated by this data set, the GC and Bath Analyzer measurement techniques accurately measured the concentration. The Flowsensor measurement was within 1.6% of the known concentration at 10% percent concentration and above.

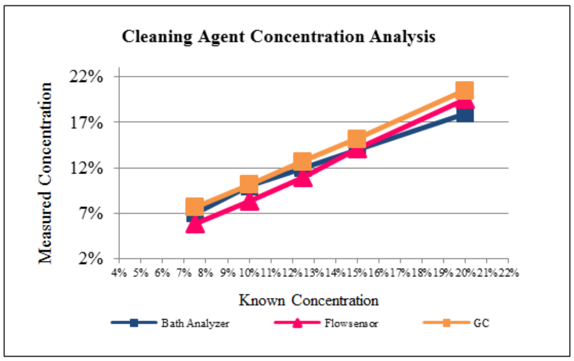

Figure 5. GC, Bath Analyzer & Flowsensor test data – Known concentration

RMA Flux Load Analysis (micro phase cleaning agent)
Utilizing a batch cleaner, the wash tank was filled with fresh Cleaning Agent to an initial concentration of 15% as verified by Refractive Index, Bath Analyzer and Flowsensor. The cleaner basket remained empty as this test examined the effect of flux load on concentration measurement only.

For this test, high solid content RMA liquid flux was sourced. Concentrated liquid flux was used in order to minimize the overall flux volume required. To create the concentrated flux, liquid flux was evaporated such that the volume was reduced until it reached the known solid content. In this case, the liquid flux solid content was 33%.

Following cycle start, flux was added, concentration measurements were taken, then diluted, and concentration re-measured employing Refractive Index and the Bath Analyzer. The Flowsensor continuously recorded the wash bath concentration throughout the test.

The initial wash bath concentration measured by Refractive Index and Bath Analyzer was confirmed at 15% concentration.

Flux was added to a concentration of 1% by volume. During this wash cycle, the Flowsensor measurements remained fairly constant throughout (Figure 6). At time t_2, the Bath Analyzer measurement remained accurate, yet the Refractive Index measured 22% (actual 14%). The wash bath was then diluted with DI-water. The Flowsensor measured 7% as also indicated by the Bath Analyzer, yet the Refractive Index measured 15%.

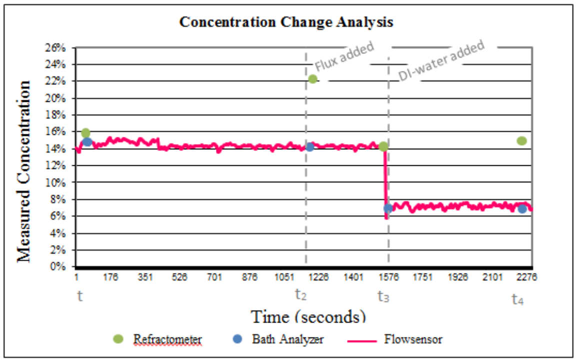

Figure 6. Concentration Change Analysis

As expected, in the presence of flux residue, the Refractive Index reading overstated the wash bath concentration in both instances. At a 1% flux load, both the Flowsensor and the Bath Analyzer accurately indicated the wash concentration even as it was diluted by half.

Methodology
Having established the performance of the Flowsensor as an accurate concentration monitoring technology, the authors selected two beta sites, described as A & B for detailed field evaluation. Two versions of the Flowsensor were employed at the beta sites. The Flowsensor type was installed in each location and concentration data monitored, recorded and analyzed throughout the beta test period.

Beta Site A - Flowsensor: Wash Bath Concentration Monitoring

Preliminary data (four days) from this beta test site was presented in the SMTAI 2013 paper [1]. However, in this paper, 20 days of field data are presented.

Customer description:

- Global security and aerospace company principally engaged in the research, design, development, manufacture, integration and sustainment of advanced technology systems, products and services

Flowsensor type evaluated:

- Inline Flowsensor with continuous concentration monitoring and display. The process required manual DI-water and cleaning agent concentrate make-up.

Beta Site B - Flowsensor CLC: Wash Bath Concentration Monitoring and Closed Loop Control
Customer description:

- Contract manufacturer that provides design, engineering, system integration, and testing services to industrial, energy, medical, defense, and aerospace segments of the electronic manufacturing services industry

Flowsensor type evaluated:

- Inline Flowsensor with continuous concentration monitoring and display complete with automated DI-water and concentrate makeup
- This system is integrated with the inline wash section pump. That is, whenever the wash section pump is actuated, wash bath flows through the Flowsensor CLC system. Concentration measurement is logged and wash bath makeup consisting of DI-water or concentrate cleaning agent is automatically added as required.

Data Review – Beta Site A

In this case, the customer had a qualified cleaning process for many years utilizing an inline spray-in-air cleaner. The process parameters are detailed in Table 1.

Table 1: Inline Cleaner Operating Parameters

Cleaning agent type:	Micro phase cleaning agent
Flux types:	RMA and No-Clean
Wave Flux type:	No-Clean
Cleaner type:	Spray-in-air inline
Wash solution temperature:	140°F
Target concentration:	10% to 16%
DI-water make-up:	Manual
Flowsensor type:	Inline – concentration indication

Upon installing the Flowsensor, fresh wash bath was added and the concentration adjusted to the 12% target. As the customer monitored the concentration via the Flowsensor controller, DI-water and/or cleaning agent concentrate was added using a dosing pump that was manually actuated as required. For the duration of the test period, the wash bath was not changed.

Throughout the test period, the customer extracted bath samples daily. The Flowsensor concentration, as indicated by the controller, was recorded on the bottle and the sample returned to the ZESTRON Technical Center for further evaluation.

At ZESTRON, the bath sample was analyzed by refractometry (BRIX) and the Bath Analyzer. These data points, as well as the Flowsensor concentration value as indicated on the bath sample by the customer, were plotted and is detailed in Figure 7.

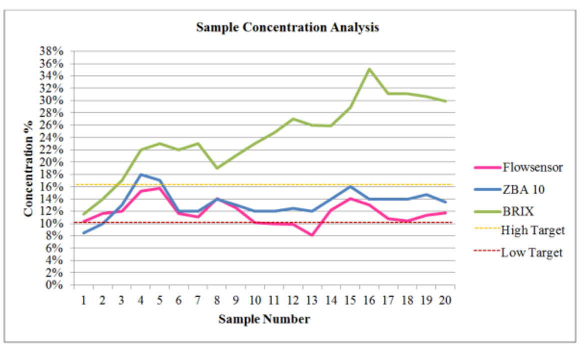

Figure 7. Beta Site A - Concentration Data Comparison

Results
In this case, the concentration target was 12%. As DI-water and concentration make up was added manually, the actual concentration varied from 10% to 16%. The Bath Analyzer and the Flowsensor results mirrored each other. However, Refractive Index overstated concentration with increasing error as testing progressed. The authors attributed this increasing error to the increased wash bath contamination.

Data Review – Beta Site B
This customer had a qualified inline cleaning process that ran 10 to 12 hours a day. Prior to installing the Flowsensor CLC system, concentration was monitored using the Bath Analyzer. The line operator spent more than half of his time monitoring and adjusting wash bath concentration adding DI-water and/or cleaning agent concentrate as required.

The process parameters are detailed in Table 2.

Table 2: Inline Cleaner Operating Parameters

Cleaning agent type:	Dynamic surfactant cleaning agent
Flux types:	RMA, RA, WS
Wave Flux types:	RMA, WS
Cleaner type:	Spray-in-air inline
Wash solution temperature:	150°F
Target concentration:	20%
Flowsensor type:	Flowsensor CLC

Following installation of the Flowsensor CLC, fresh wash bath was added and the concentration adjusted to 20%. The concentration range of the Flowsensor controller was set to ±2%. The control system monitored wash bath concentration and added DI-water and concentrate as required in order to maintain the desired concentration range. Onsite concentration data recorded by the control system is plotted in Figure 8.

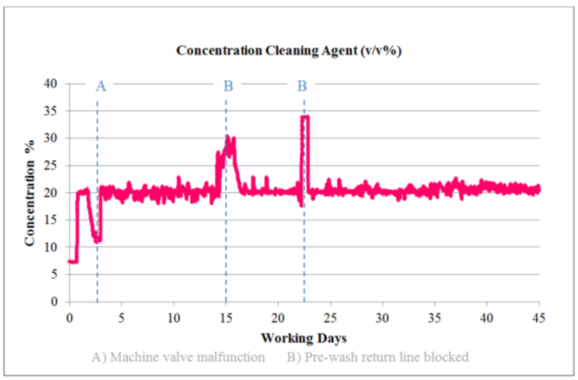

Figure 8: Flowsensor concentration measurement

Data presented in Figure 8 represents 45 working days (10 weeks) of continuous operation without a bath change. During this time, three deviations are indicated.

As can be seen, the Flowsensor CLC system captured concentration deviations and the time period such that this data could be correlated with other process control data points and that any corrective action deemed necessary could be taken.

Throughout the test period, the customer extracted daily bath samples. The wash bath concentration, as indicated by the CLC system, was recorded and the sample returned to the ZESTRON Technical Center for further evaluation.

At ZESTRON, the bath sample was analyzed by refractometry (BRIX), the Bath Analyzer and GC (Gas Chromatography). These data points, as well as the CLC value as indicated on the bath sample by the customer, are plotted in Figure 9.

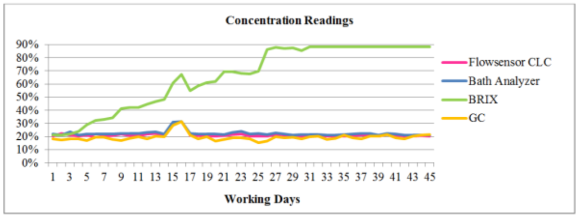

Figure 9: Beta Site B - Concentration Data Comparison

From this figure, one can observe the following:

- As wash bath contamination increases, Refractive Index increases
- The high concentration reading (Day 15) reflects the same error indicated at point B of Figure 8
- The Bath Analyzer, GC and Flowsensor results mirror each other indicating accurate concentration measurement and control

As detailed in Figure 8, the wash bath concentration, as controlled by the Flowsensor CLC system, remained steady throughout the test period. In this case, the deviation from concentration set point was much smaller as compared to Beta Site A (Figure 7). This is attributed to the automated control of DI-water and concentrate addition. It was certainly expected that wash bath contamination was increasing even though concentration level remained within the process specification. Thus, the authors decided to evaluate NVR as a measure of wash bath contamination.

NVR was determined employing a standard technique of adding a known amount of sample to a pre weighed evaporating dish. The dish was placed in a 200°C oven for approximately 3 hours or until fuming stopped, leaving solids residue remaining. The NVR analysis was conducted at the ZESTRON Technical Center using the daily samples obtained from the beta site. As anticipated, NVR values gradually increased as the test progressed. The NVR analysis was based on wash bath samples received from start up through day 45. The results in Figure 10 indicate that the NVR value steadily increased to approximately 7.5% over the 45 day test period. It is interesting to note that that even though the NVR value increased more than sevenfold, the Flowsensor CLC was able to measure and maintain concentration accurately.

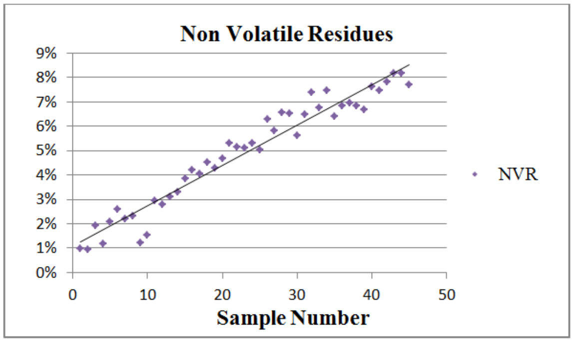

Figure 10: Non Volatile Analysis

Conclusion

In this study, the Flowsensor or acoustic concentration measurement system that was first introduced at SMTAI 2013, was further evaluated at the original beta site detailing 20 days of concentration monitoring data. At this site, the electronic assembly process utilized RMA flux and a cleaning process based on a micro phase cleaning agent.

Additionally, the Flowsensor CLC or closed loop concentration monitoring and control system was installed at a second beta site and evaluated over a 45 day period. At this site, the electronic assembly process utilized both RMA based and water soluble flux and a cleaning process based on a dynamic surfactant cleaning agent.

Upon review of the beta test data, the Flowsensor employed at Beta Site A was found to accurately indicate wash bath concentration while the Flowsensor CLC, employed at Beta Site B, was found to accurately indicate and control wash bath concentration, each throughout the test period. In each case, the Flowsensor concentration data was compared with established measurement methods in order to confirm process accuracy.

With any electronic substrate cleaning system, wash bath contamination accumulates over time, principally in the form of flux residues. The ability to determine accurate concentration measurement in the presence of contamination is critical to any monitoring and control system. Using bath samples collected from Beta Site B and a contamination analysis based on NVR, this study verified that acoustic measurement technology, employed in the form of the Flowsensor CLC within this study, can accurately indicate and control wash bath concentration in the presence of flux residue.

Authors

Umut Tosun, M.S.Chem.Eng., is the Application Technology Manager at ZESTRON America. Questions and comments can be addressed to umut.tosun@zestronusa.com.

Axel Vargas, is an Application Engineer at ZESTRON America. Questions and comments can be addressed to mailto:axel.vargas@zestronusa.com.

Bryan Kim, Ph.D, is the Director of Engineering at Pressure Products Company, Inc. Questions and comments can be addressed to bhkim@pressureproducts.com.

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