Evaluating Process Control Test Methods in Establishing Process Limits Process Control in Surface Finishing: Part I

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Surface finishers use a variety of chemical and physical tests to monitor and control wet processes. Common test methods are normally specified by process chemistry suppliers or derived from generic test methods listed in various industry guidebooks. These sources provide little discussion on the background of the method. Process solutions are normally made up to a target concentration and a control range is established. The analytical frequency required to maintain a solution within the control range is a function of the contamination rate; the consumption rate of the various solution constituents due to plating, dragin, dragout, evaporation, and chemical reactions; and the required control range. Unfortunately, the accuracy and precision of the various test methods are not well defined and control ranges normally neglect these factors. This paper reviews some common test methods used by surface finishers and presents data on the accuracy and precision of these methods. A general methodology for evaluating and improving the capability of analytical methods and a procedure for establishing appropriate control limits are discussed.

1.0 Introduction

Chemical, instrumental and physical testing methods are the primary tools used by surface finishers to monitor and control chemical processes. These analytical methods are relatively quick and simple and provide analytical data necessary to control solution concentration and impurities. Various test methods are regularly utilized in the surface finishing laboratory and may include titrametric analysis, gravimetric analysis, volumetric analysis, pH, colorimetric tests, coating stress tests, and Hull cell tests. Additional tests include porosity, salt spray, coating weight, adhesion, coating thickness, Taber abrasion resistance, and hydrogen embrittlement. Some tests are pass/fail while other results must be quantified and potential errors understood to evaluate their accuracy for comparison to acceptable parameter value ranges. Common chemical test methods are available in a number of industry handbooks, and chemistry suppliers normally specify test methods for proprietary solutions. Experienced chemists will often derive specific test methods and source, the limits of the test procedure must be defined and documented for effective process control.

The instrumental and physical test methods are beyond the scope of this paper. Guidance on the accuracy and precision of wet chemical tests is not easy to find. Common test methods are generally presented as recipes with little discussion on chemical or physical basis of the method or calculations. Discussion of the limitations of the test methods with regard to concentration range and method interferences are also normally absent. Unfortunately, the accuracy and precision of the various test methods are also not well defined, and established control ranges normally neglect these factors. The result is that surface finishers often believe that processes are in control when they are not (false accuracy, poor performance) or unnecessary additions and deletions are prescribed (poor economy). Method users generally trust that the method provides good data and rarely ask questions about the precision and accuracy for the method.

Effective surface finishing requires that process solutions be controlled within the prescribed concentration range. Both desirable and undesirable chemical constituents must be controlled. The operating concentration range is based upon process performance, and if a wide concentration range ($\pm 20\%$) yields consistently acceptable performance, it is not necessary to arbitrarily narrow the concentration range, although it may be desirable to operate at the low end of the range to minimize dragout losses. If the process control range is narrower, then there must also be consideration of the test method accuracy and precision. Effective process control requires capable test methods. Capable test methods are accurate and precise within a prescribed range and the data produced is acceptably reliable. The required analytical frequency is a function of the solution depletion or contamination rate, which is impacted by workload, evaporation, dragin, dragout or side chemical reactions. Additions or deletions (decant/bleed or dump) are prescribed on the basis of the analytical data. With capable test methods, reliable

historical data, effective solution maintenance and a reliable production basis, statistical process control (SPC) methods can be utilized to decrease analytical frequency and/or improve process control. With SPC small frequent additions and/or deletions are prescribed statistically and analytical data is used to "tune" the solution.

This paper reviews some common analytical methods used by surface finishers and discusses the accuracy and precision of these methods. This paper presents data from recent projects where analytical labs were commissioned and operated to control surface finishing processes for aerospace and general manufacturing plants (4). In addition, a general methodology for evaluating and improving the capability of analytical methods and a procedure for establishing appropriate control limits are discussed.

2.0 Accuracy, Precision and Error

All measurements have error or uncertainty. The errors arise from limitations of the measuring device, the technique, or from the analyst's ability to recognize a physical change that is part of the analysis. Statistical analysis provides many tools to evaluate the data collected. However, complex analyses are generally employed when simple ones fail. For laboratory methods, the simplest evaluation of error involves examining the precision and accuracy (5, 6) of the method.

Precision is how close together a group of measurements are to each other (e.g. - data result variations from a split sample analyzed more than once by one or more analysts). The relative variation provides a measure of the precision of a measurement (Equation 1). The relative variation for a specific result is calculated from the difference between the measurements compared to the mean of all the measurements in a given set of measurements where X_m is the value measured.

$$\frac{\text{Mean} - X_{\text{m}}}{\text{Mean}} \times 100 = \% X_{\text{m}}$$
(Eq 1)

Precision of a group of three or more measurements is calculated as the relative standard deviation:

$$RSD = (\mathbf{k} \ \overline{\mathbf{y}}) \times 100 \tag{Eq 2}$$

Where:

RSD = relative standard deviation s = standard deviation = mean of replicate analyses Standard deviation, s, is defined as follows:

Where:

S	=	standard deviation
	=	measured value of the ith replicate
	=	mean of replicated measurements
n	=	number of replicates

Evaluating precision indicates how consistent a measurement is but, this information does not necessarily mean the measurement is accurate. Furthermore, if the method used cannot be compared to the actual value, only the precision can be estimated. At this point, more sophisticated statistical analysis must be used to attempt to validate the data. Statistical analysis relies on collecting enough repeatable data such that the observed variation can be accounted for by indeterminate error. Indeterminate errors result from variables that are not, or cannot be, controlled. In well-designed test methods, the indeterminate error will result in small changes to the values measured. Variation in the measurements can then be assigned to changes in the level of the measured parameters. This typically requires a large amount of data collection for a given analysis. From this set of data, the standard deviation and the sample size needed to establish a high (90% or better) confidence in the measurements can be calculated. Gathering and logging regular process control data allows valid calculations to be made. Graphical data tracking and statistical procedures and/or software can facilitate error calculation and evaluation. However, when a process control laboratory is being established, waiting several months to collect sufficient data and determine if the data is valid is impractical for establishing control limits. It is important to quickly develop confidence that the methods and data are good and that the data accurately reflect actual process solution parameters. Testing solutions with known concentrations can help establish initial process control ranges.

(Eq 3)

Accuracy is how close the measured value is to the actual value. It is possible to make measurements that are very precise but highly inaccurate due to one or more systematic errors causing an offset. If the systematic error factors are evaluated, the offset can be fixed or appropriate measurements of the results can be consistently adjusted to account for the offset. The simple analysis of accuracy is completed by using the relative error (equation 4) where X_m is the value measured and compared to the actual value.

$$\frac{\text{Actual} - X_{\text{m}}}{\text{Actual}} \times 100 = \% \text{ Error of } X_{\text{m}}$$
(Eq 4)

When measurements are made, it important to understand the errors and to minimize their

influence on the analytical results. Typically, analyses are structured so that the measurement error in sampling and analysis is much less than the method error. It is still important to consider the sources of error and how they affect the accuracy and precision of the method employed.

As an example, consider a titration that might employ each of the measurement devices listed in Table 1. This titration tests a 10 ml sample of nickel sulfate against 0.10 M EDTA (29.2 g/L). 15.1 ml of EDTA solution is used in the titration. Table 1 shows that the measurement error used to make-up the EDTA titrant are much less than measurement error in sampling or testing the solution. As shown in Table 1, doubling the sample size with a similar pipet error (+/- 0.01 ml) reduces the sample error by a factor of two. The titration error is also reduced by a factor of two, as twice as much solution is sampled and twice the titrant is required with the same measurement error. Equation 5 shows the calculation of the nickel contained in the solution. 8.8 g/L Ni are reported as the result of the titration. From Table 1, the error in the titration is 0.33 %. This indicates that the result is within +/- .03 g/L of the value reported. If the 20 ml sample is used, then the error drops to 0.16%.

<u>0.0151+ (0.10 Mole/L)</u>	x 58.7 g/Mole = 8.8 g/L	(Eq 5)
0.010 L		

Item	Size	Accuracy	Error Introduced
Analytical Balance	NA	+/- 0.0001 g	0.0003 %
Volumetric Flask	1 L	+/- 0.0002 L	0.0002 %
Pipet	10 ml	+/- 0.02 ml	0.2%
Pipet	20 ml	+/- 0.02 ml	0.1%
Buret	15.1	+/- 0.05 ml	0.33%
Buret	30.2	+/- 0.05 ml	0.16%

Table 1Common Laboratory Device Errors

The error analysis neglects a key observation that even though the error in each portion of the measurement can be measured, the total error actually measured is often much larger than expected. This is due to a number of factors that are difficult to quantify. Specifically, there are always variables that are not, or cannot be, controlled. For example, there can be interfering species in the test solution. The analyst's perception of the end point may differ from other analysts'. For some analyses, temperature affects the result, and failing to adequately cool a hot sample, as well as daily and seasonal variations in room temperature, can change results. Also, the reaction time or an excess quantity of reagent can affect the results for a particular analysis.

3.0 Chemical Tests and Errors Involved

Perhaps the most common test used in the laboratory because of its simplicity and wide range of applicability is the titration. The vast majority of process control tests are performed using some sort of titration. Titration uses the basic principal of equivalence to equate a known amount of a solution of unknown concentration with a known amount of a solution with a known concentration. Most metal finishers are familiar with acid-base titration. In order for the reaction between an acid and a base to be observed visually, an indicator must be used. Indicators also behave as an acid or a base with at least one of the forms being highly colored. Key to the accuracy of the titration is selecting a suitable indicator. If the acid-base reaction is plotted as a function of pH and volume of base added, a typical curve will appear as shown in Figure 1. The two curves represent two different titrations and illustrate one of the necessary characteristics to select the proper indicator. Curve A represents the titration of 50 ml of 0.1 N HCl with 0.1 N NaOH. Curve B represents titration of 50 ml of 0.001 N HCl with 0.001 N



Figure 1: Plot of pH versus volume of titrant added.

NaOH. The labeled areas show the pH range for the indicator transition. For curve A, any of the indicators provide a clear color change; however, for curve B, only the bromthymol blue provides a sharp change. The very gradual change shown for the methyl orange transition would make it very difficult to determine the endpoint consistently. Typically, an indicator with a sharp transition is desirable. Sometimes an indicator at the extremes of the transition is used to avoid

a competing side reaction. For example, titrating an acid with a high metal load, such as a pickle solution, using phenolphthalein indicator could lead to precipitation. The pH transition is above the point where iron will begin to precipitate (8). Using methyl orange avoids the precipitation since the endpoint transition is still slightly acidic and the metals remain dissolved.

A list of common indicators and the pH of their color transition is shown in Table 2. Selection of the proper indicator is used to produce a clearly defined endpoint either as a result of the specific acid/base property or to minimize the effect of interferences. If a very gradual endpoint color change is observed, several possible solutions exist to improve the endpoint. The first step is to generate a graph similar to Figure 1. Ideally, the transition will be vertical, or nearly vertical, as shown. As the curve of pH versus addition of the titrant becomes less vertical, the endpoint will become harder to detect with good repeatability. It is possible that the wrong indicator was chosen.

Indicator Name	Transition Range pH	Acid Color	Base Color
Methyl Violet	0.5-1.5	Yellow	Blue
Methyl Orange	3.1-4.4	Red	Yellow
Bromcresol Green	3.8-5.4	Yellow	Blue
Bromthymol Blue	6.0-7.6	Yellow	Blue
Methyl Red	4.2-6.3	Red	Yellow
Cresol Purple	7.4-9.0	Yellow	Purple
Phenolphthalein	8.0-9.6	Colorless	Red
Thymol Blue	8.0-9.6	Yellow	Blue

 Table 2

 Common Acid/Base Indicator Properties

Overlaying the transition range on the pH versus volume added curve will clearly show if other indicators can be investigated. It may also be that the solution is buffered. Buffers are weak acids and bases that easily exchange between acid and base form depending on the hydrogen ion concentration present. Buffers act to resist pH changes over a narrow range of pH. They have stable acid and base forms. A small addition of acid causes a shift to the base form to counteract the addition. Likewise, a small addition of base would cause a shift to the acid form. If the indicator chosen has a transition within the buffer range, the color change will not be an accurate measure of the endpoint. Buffering generally occurs at a specific pH for the system. Boric acid is a great example of a buffer chemical. If enough acid or base is added the buffer can be overpowered but the concentration of the buffer species affects the apparent concentration of the other species detected. In some instances, using a pH meter and titrating to 7.0 provides the most accurate determination of the endpoint. This adds complexity to the experiment and is usually not necessary.

Another commonly used titration is the complexometric titration. This titration is used to determine metal ion concentration with standard EDTA solution. EDTA is a complex organic molecule that forms several bonds with the metal cation. Unlike acid-base titration where buffering can obscure the endpoint, EDTA titrations need to be buffered because the formation of the specific EDTA-metal complex is pH dependent. Table 3 lists several common metals and the minimum pH for complete formation of the metal-EDTA complex to occur. Complexometric titrations also require an indicator. These indicators also form complexes with the metal but the metal is more weakly bound, and a slight excess of EDTA scavenges the metal from the indicator complex, causing a color change. Most dissolved metals can be measured using EDTA titration. The Table 3 data show a similar pH minimum for the metals. Significant impurity levels of other metals can interfere with the accuracy of this titration.

Table 4 lists the weight equivalents for common metals titrated with 0.1 M EDTA. The atomic weights are also listed. Of the metals listed, all but silver have a molar equivalent ratio of 1:1. The molar equivalent ratio for silver is 2:1. With the proper indicator, the relationship between the equivalent species is shown in equation 6.

Species	Minimum pH for EDTA Titration				
Fe ⁺³	1.8				
Ni ⁺²	3.9				
Cu ⁺²	3.9				
Cd^{+2}	4.3				
Zn ⁺²	4.0				

 Table 3

 Minimum pH for EDTA Titration of Various Metals

Table 4					
EDTA Eq	uivalents for	Select Metals			

Metal	Atomic wt	Equivalent/ ml 0.1 M EDTA (mg)
Aluminum	27.0	2.7
Cadmium	112.4	11.2
Copper	63.5	6.35
Iron	55.8	5.58
Lead	207.1	20.7
Nickel	58.7	5.87
Silver	107.9	21.6
Tin	118.7	11.9
Zinc	65.4	6.54

Conc Sample
$$(g/L) = Conc Titrant (Moles Eq/L) \times Vol Titrant \times Molecular Wt Sample (Eq 6)Vol Sample$$

Errors in titration generally arise from interferences from other titrateable species. One of the other key errors can be the misapplication of the method or its assumptions. Multiple acids, multiple bases or large levels of contaminant metals can lead to errors. An example that demonstrates many of the principals and the limitation is the analysis of a simple cleaners composed of sodium hydroxide, tri-sodium phosphate (TSP) and sodium meta-silicate (Meta). Table 5 shows the composition of two different cleaners. Both tri-sodium phosphate and sodium meta-silicate generate caustic soda when hydrolyzed by water, as shown in equations 7 and 8.

$$Na_{2}SiO_{3} + 2H_{2}O = 2NaOH + H_{2}SiO_{3}$$
 (Eq 7)

$$Na_{3}PO_{4} + H_{2}O = NaOH + Na_{2}HPO_{4}$$
(Eq 8)

Analysis of the solution is done in two steps; 1) the solution is titrated against standard HCl with methyl orange indicator. 2) The resultant solution is boiled, then back-titrated with standard NaOH using phenolphthalein. The following chemical reactions occur when the compounds are titrated with HCl:

$$NaOH + HCl = NaCl + H_2O$$
(Eq 9)

$$Na_{2}SiO_{3} + 2HCl = 2NaCl + SiO_{2} + H_{2}O$$
 (Eq 10)

$$Na_{3}PO_{4} + HCl = Na_{2}HPO_{4} + NaCl$$
 (Eq 11)

$$Na_{3}PO_{4} + 2HCl = NaH_{2}PO_{4} + 2NaCl$$
 (Eq 12)

$$NaH_{2}PO_{4} + NaOH = Na_{2}HPO_{4} + H_{2}O$$
 (Eq 13)

From equations 9-12 the HCl neutralizes all of the alkaline species. The first titration determines the total alkalinity. Boiling causes the silica to precipitate and titrating with NaOH and phenolphthalein causes reaction 13 to occur. The use of phenolphthalein is crucial since the pH of the phenolphthalein transition provides conditions that strongly favor the forward reaction in equation 13. This particular method is described in a government document (TO 42C2-1-7), and the following equations are used to estimate the levels of each compound:

NaOH (g/L) = vol HCl x normality of HCL x 3.68	(Eq 15)
TSP (g/L) = vol NaOH x normality NaOH x 8.55	(Eq 16)
Meta $(g/L) = (Total Alk - (NaOH + TSP))$	(Eq 17)

The factors used in each equation take into account the sample size, the molar equivalence and the conversion from moles to grams of the substance. The key assumption is that the sodium hydroxide concentration remains essentially constant. The calculations use the same titration with a different factor to estimate both the total alkalinity and the sodium hydroxide content. In Table 5 the cleaner with the higher sodium hydroxide content has a molar ratio of the NaOH to the other components of roughly 20:1. For this cleaner, the method does fairly well. The error shown is less than 10%. However, the method fails miserably for the second cleaner; the molar ratio is slightly above 2:1 and the method is not able to distinguish between sodium meta-silicate and sodium hydroxide. The government document recommends the same method for both cleaners. In this instance, the method originally called for is misapplied. In order to measure the low NaOH cleaner, another step is needed to actually measure the sodium meta-silicate concentration.

Chemical	Cleaner 1 g/L	Conc Reported	% Error	Cleaner 2 g/L	Conc Reported	% Error
NaOH	75	76	1.4	7.5	25	333
Na ₃ PO ₄	15	14	6.7	15	14	6.7
Na ₂ SIO ₃	26.4	26	1.6	26.4	1.5	94.3

Table 5Cleaner Compositions

The alternate method begins as the original by determining the total alkalinity of the sample with standard HCl. The sample is then boiled to precipitate the silica and back titrated with standard NaOH to determine the TSP concentration. A separate sample is digested with strong acid to precipitate the silica. The silica is gathered by filtration, washed, dried and weighed. From the weight of silica collected, the molar amount of sodium meta-silicate is estimated. In this way the TSP and sodium meta-silicate are measured directly. The sodium hydroxide is estimated by subtracting the molar quantities of TSP and sodium meta-silicate from the total alkalinity (Eq.18).

NaOH (g/L) = Moles
$$Eq_{Total Alk} - (3 \times Moles TSP + 2 \times Moles Meta)$$
 (Eq 18)

The chemistry discussed earlier that demonstrated that three moles of hydroxide are available

from TSP and two moles are available from sodium meta-silicate, require the factors seen in equation 18. Implementing the method improved the method accuracy for Cleaner 2 in Table 5. The resultant method error seen was in the same range as the original method for the more concentrated cleaner (Cleaner 1).

4.0 Method Accuracy

Table 6 lists several analyses and the measured error for each analysis. The theoretical error listed is the sum of the component errors, including the sample volume error, any dilution error, titrant concentration error and the titration error. The measured error is assigned by evaluation of a stock solution using the method and calculating the % variation from the actual concentration. Where possible, solids were weighed and used to make the stock solutions and 1 liter of each solution was made in a volumetric flask. Liquid acids used were laboratory grade.

Species/Solution	Method	Conc. (g/L)	Theoretical Method Error %	Measured Error %	
Nickel (Watts)	EDTA titration	52	1.4	1.5	
Nickel (Sulfamate)	EDTA titration	85	1.8	2.0	
Nickel (EN)	EDTA titration	5.2	1.3	1.3	
Cadmium	EDTA titration	22.5	1.1	1.5	
CrO ₃ (Chromium Plate)	Thiosulfate Titration	247	1.0	8.8	
CrO ₃ (Chromic Acid Anodize)	Thiosulfate Titration	48 1.5		4.3	
Cyanide (Cadmium Plate)	AgNO3 titration	100	1.4	2.0	
Boric acid (Nickel Sulfamate Plate)	HCl Titration Mannitol	50	3.5	10	
HCl Pickle	NaOH titration	82	1.0	8.2	
H ₂ SO ₄ Pickle	NaOH	176	1.0	9.7	
H_2SO_4 (Anodize)	NaOH	165	1.5	5.7	
Aluminum (Anodize)	Total Acid	0.1	1.5	7.0	
Oxalic Acid (Hard Anodize)	KMnO ₄ titration	15	0.7	4.6	

Table 6Method Accuracy for Select Species

Nickel Analysis

Nickel measurements from three different solution types were considered. The evaluation of the nickel content was done by the same method. The sample pH was raised by the addition of concentrated ammonium hydroxide. The sample was titrated with EDTA solution in the presence of murexide indicator. The only difference in the analysis of the three solutions is that a larger sample was used for electroless nickel solution due to a significantly lower nickel concentration range. From Table 6, the actual measured errors track very closely to the theoretical errors and are relatively small. The EDTA titration method is very effective at analyzing nickel from various solution forms.

EDTA Metal Analysis

Also listed on Table 6 is the analysis of cadmium by EDTA titration. The cadmium analysis is similar to the nickel analysis as the pH of the solution is raised by adding a pH 10 buffer that is a mixture of ammonia and ammonium chloride. Comparing the error of cadmium analysis with the nickel analysis, EDTA titration worked well with both. Additionally, though not listed in Table 6, zinc and copper analysis by EDTA titration were also tested and calculations showed comparable errors to those listed for cadmium and nickel. The method is very reliable as indicated by the low method errors reported.

Chromic Acid Analysis

Chromic acid content is measured using titration against standard sodium thiosulfate solution. In this titration ammonium bifluoride and concentrated hydrochloric acid are added to lower pH. Then potassium iodide is added. The hexavalent chromium oxidizes the iodide to free iodine. The iodine is detected using starch indicator by titration with thiosulfate. The high concentration of the chrome plating solution requires a dilution and this increases error. The reaction releasing iodine takes a few minutes and incomplete reaction will also increase error as will the presence of other oxidizeable species. The overall error measured for this analysis was 8.8 %.

Also considered is the similar analysis of a chromic acid anodizing solution. Here the chromic acid content is roughly 20% of that in the plating solution. A smaller dilution is used and similar amounts of acid, bifluoride and potassium iodide. The lower concentration insures a quicker reaction and probably is the reason in the improvement in the measurement error shown in Table 6. Analysis by this method is acceptable at measuring chromic acid.

Cyanide Analysis

Although use of cyanide processes is decreasing, there are still hundreds of users in the industry.

This titration is used for all the cyanide-containing plating solutions and exhibits similar accuracy with all. The solution is buffered with ammonia and potassium iodide is added as the indicator. The solution is then titrated to a yellow endpoint with silver nitrate. For this analysis method, the measured error compares well with the theoretical error.

Boric Acid

The method used is the mannitol paste sodium hydroxide titration. The sample of solution is made into a paste by mixing with mannitol powder. The indicator is added and titration is done with 1 N NaOH. The errors in this method arise from limiting the amount of water in the experiment. When the sample volume is too large and/or the titrant too dilute, the endpoint becomes obscured due to excess water volume in the paste. Success is seen with small solution samples requiring a few milliliters of titrant. Measurement error increases because of the small amount of titrant used and the small sample size.

Acid Analysis

Although acid-base titration is one of the simplest analyses, the measured error is relatively high compared to other methods. Acid solutions are made up by dilution of concentrate and the error probably reflects the variability of the technical grade acid rather than error in the method. Titration of technical grade hydrochloric acid with standard NaOH revealed that the acid used for solution make-up was actually less than the 12.4 molar seen for laboratory grade acid. Recalculation of the error based on the actual acid concentration lowers the method error to 2.5%. It is important to understand the error introduced from the variation of make-up acid concentration, since additions prescribed by this analysis will result in solution concentrations that are slightly different than expected. This variation is not a result of the method, but a result of the make-up chemical variation.

Anodizing Solution Analysis

Anodizing solutions are often analyzed by a two-step titration. In the first step, the free acid content is measured. In the second step, the total acid as sulfate is measured. In the anodizing solution the dissolved aluminum will exist as aluminum sulfate. The difference between the free acid content and the total sulfate content is the aluminum metal content. Tracking aluminum is useful as some aluminum improves the process and leads to more consistent performance in the coating formation and in the ability to dye and seal the coating formed (9). Too high an aluminum content reduces the solution conductivity. Table 5 lists a *negative* concentration for aluminum. The problem with this anomalous data point is that at very low levels of aluminum the sampling and analysis error can lead to a slightly larger titration volume for the free acid than for the total acid. In this particular case, the anodizing solution is relatively new and has

seen little work. The actual aluminum content is near zero. Six titrations of the solution were completed for both free acid and total acid. Two of those titrations show a slightly larger free acid titration volume (0.1 ml). Stock solutions with dissolved aluminum content at 0.5, 1.0 and 5.0 g/L aluminum were prepared and analyzed by the method, and in each of these instances, the dissolved aluminum was measured with acceptable accuracy (+/- 7%). The limitation of this method is that at low dissolved aluminum levels, the method can produce a negative result. Using a larger sample or a more dilute titrant does not improve the method because no matter what sample size or titrant concentration, there will always be a minimum aluminum concentration where the experimental error could produce a negative result. Therefore, as long as the experiment results show good precision, a slightly negative result is assigned a zero aluminum content. For many anodizers, this is not necessarily an issue because on make-up of a new solution, aluminum is added to condition the solution to the range of 2-4 g/L, and in this range the method performs acceptably.

5.0 Aligning Process Control Ranges with Method Limits

It is very important to establish process control operating range limits that insure a particular process is in the right chemical condition to perform adequately. One key part is the operating range for a process tank. From a purely theoretical standpoint, the control limits should be defined to insure consistent production of the parts produced. Although experienced operators may optimize solution operating and control ranges based upon observation and objectives, a relative minority of facilities undertake the effort necessary to determine the operating limits for their particular set of conditions. Most facilities adopt limits based upon outside specifications. The operating range affects a number of factors aside from product quality. Other factors that must be considered include chemical solubility, waste treatment impacts, operating solution conductivity, and process energy efficiency. Some specifications provide detailed guidance on the operating range while others provide little guidance other than the optimum operating concentration. In the case of a vague optimum concentration, the user must set the operating range; ± 10 or 20 percent is a common arbitrary control range.

Before setting the operating range for a process, the analytical method error must be considered along with the target absolute operating range limits. If the control limits suggested are necessary, then the analytical method and errors must allow for monitoring the process to stay within those limits. As shown in Figure 2, the analytical method error range effectively reduces the solution concentration monitoring and control range needed to stay within the established absolute control range limits. Adjusted process monitoring and control ranges to stay within absolute control range limits are calculated for specific solutions in Table 7. The data is based on field measurements of solution specific/constituent specific parameters and corresponding error analysis computations. The reduction of the process control range adjusted for the method error

is shown in Table 7. These results indicate the control range is only slightly reduced for each of the nickel measurements and many other processes listed in the Table. For other solutions, other factors are involved in the setting the limits.



Figure 2: Impact of analytical error on narrowing of process control limits

Table 7 shows that the analytical method error has a major impact on the hard chrome plating control range. The listed ± 22 g/L concentration range is reduced to ± 1 g/L due to nearly 10 % error in the analysis method. This means that unless the measurement is the set point. the method error could place the actual measurement outside the control range. Preceding sections of this paper discussed that statistical methods are employed where simple ones fail. This chrome plating example is a case where statistical methods need to be employed over a long period of time to establish the long term accuracy of the method and allow the use of a reasonable control range. Another interesting case is seen by reviewing the cadmium and cyanide control limits. In this case, another factor is used to assign the control range the factor is the ratio of cadmium to cyanide. Experiments showed that a 5:1 cyanide to cadmium ratio produced the broadest current range for acceptable plating. To maintain a close tolerance on the ratio, the cadmium is controlled closely to limit the fluctuation of the cyanide concentration. Fortunately the metal concentration changes quite slowly and control within the range is not difficult. The boric acid range is also of interest. In this case the set point is determined by the solubility of boric acid at the 55 °C operating temperature. The range is narrow to insure that the boric acid level is soluble.

Species/Solution	Concentration Range (g/L)	Measured Error (%)	Set point (g/L)	Adjusted Range
Nickel (Watts)	45-60	1.5	52	46-59
Nickel (Sulfamate)	80-90	2.0	85	81.6-88.4
Nickel (EN)	4.5-6.0	1.3	5.2	4.6-5.9
Cadmium (Cadmium Plate)	20-30	1.5	22.5	20.2-24.7
CrO ₃ (Chromium Plate)	225-270	8.8	247	245-246
CrO ₃ (Chromic Acid anodize)	30-105	4.3	48	39-57
Cyanide (Cadmium Plate)	90-130	2.0	112	100-125
Boric Acid (Ni Sulfamate Plate)	40-60	10	50	45-52
HCl (Pickle)	41-85	8.2	82	44-78
H_2SO_4 (Pickle)	92-276	9.7	176	101-249
H_2SO_4 (Hard Anodize)	105-165	5.7	135	111-155
Oxalic Acid Hard Anodize	3.5-22.5	4.6	15	3.7-21.5

 Table 7

 Method Accuracy Affected Process Range

Exceeding the solubility will lead to boric acid particles that can clog filters or cause plating roughness. The final case to discuss is the chromic acid anodizing range. The broad absolute control range supplied, with a 3.5:1 concentration variance over the control range, is reduced to a 1.46:1 concentration variance over the adjusted control range. The adjusted control range is needed to allow for maintaining the solution conductivity and voltage range, and it has the secondary effect of minimizing the quantity of chromium entering the waste treatment system from the process.

These different cases discussed demonstrate that there is no single rule that allows the proper setting of the operating range to adjust for method errors and specific process control requirements. It is however very important to examine the process control range and operating limits as carefully as the process solution chemical performance is considered. Clearly implementing the suggested control regime without an analysis of the limitations can lead to difficulties. Avoiding the difficulties comes from understanding the analyses, their limitations and how they translate into the process control measurements made in the lab. Regular review of the process control and performance data is warranted to consider adjustment of the control range to insure that the facility goals are met with each process solution on a continuous basis. Limits that are too stringent can be just as deleterious to production as those that are not tight enough.

6.0 Other Error Considerations

Evaluating the actual method error is only part of the total error analysis. Other uncontrolled errors can affect the measured accuracy in the lab. For example, laboratory stock solutions

are made up with laboratory grade chemicals and actual process solutions typically use lower purity technical grades of chemicals. Variation in the detected concentration can result from concentration or purity variations in the chemicals used. For example, acid concentrations can vary as previously discussed. Another potentially large source of error in solution make-up is from use of chemicals with differing amounts of water of hydration. For example, trisodium phosphate (TSP) used in cleaners can be purchased in anhydrous form or in dodeca-hydrate form. Misusing the hydrate form instead of the anhydrous form will result in addition of only 60% of the needed TSP addition.

Over the life of a process solution, impurities can have a significant affect on the accuracy of a method. EDTA metal analyses are a good example of this. EDTA will complex with most metals, resulting in significant build-up of contaminant metals in process solutions. This can significantly reduce the accuracy of metal analyses. Since metal impurities generally affect the plating quality at much lower levels, metal analyses can be performed over the range needed for good process control without significant errors from EDTA complexes. Contaminant build-up may also result from poor influent water quality for process solution make-up and rinses, resulting in contaminants like calcium and magnesium (these are also complexed by EDTA). Build-up in the process tank due to water evaporation could lead to reduced accuracy for the method. Due to a combination of uncontrolled and unaccounted error sources, the fractional percentage errors in typical laboratory measurements (see Table 1) may prove to be a minor part of overall observed laboratory method errors that are typically in the range of 1-10%. Specific discussion of these other error sources will be covered in a subsequent paper (Part 2) at a later date.

7.0 Summary

Good process control and product quality from surface finishing processes requires process solutions to be maintained within solution chemistry and contaminant control limits. Sampling and analytical methods used to quantify solution chemistry and contaminant concentrations have variable accuracy. The accuracy depends on solution specific parameters, additive sampling and analysis errors for each method step. Sources of error for wet chemistry analysis methods for common surface finishing process solutions were discussed. Comparative theoretical and overall measured errors were presented for selected process solutions and analytical methods. Generally the sample errors are not the significant sources of variation seen in the laboratory results. Maintaining process solutions within solution chemistry and contaminant control limits requires quantification of the overall sampling and analysis error ranges for each parameter. These parameter errors must be integrated with the respective overall parameter measurement error ranges to adjust the corresponding control ranges and process control operations. Example adjusted control ranges incorporating specific method errors were presented. Quantifying method errors for analysis of controlled parameters for specific surface finishing manufacturing processes and operation-specific production and lab conditions provides essential quantitative input necessary for maintaining parameters within process control limits and producing highquality finishes on processed parts.

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