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Improved statistical analysis of ion chromatography data from acids for aluminum anodizing solutions

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Abstract

Process monitoring and control of sulfuric and oxalic acids in aluminum anodizing solutions is necessary for producing high quality metal coatings with increased corrosion, wear and abrasion resistance. The production of military armament system parts requires narrow aluminum anodizing solution acid tolerances that increase the need for process monitoring and control. Ion chromatographic analysis is the method of choice used for these military applications. There is significant dispersion in this ion chromatographic data relative to the narrow operating tolerances. An improved ion chromatographic–statistical analysis method reruns/tests data until a specimen's results drop below a dispersion threshold relative to the narrow aluminum anodizing solution acid tolerances. This method provides acceptable process monitoring and statistical control of narrow operating tolerance aluminum anodizing solutions required for high quality military production coatings. The resultant means and improved 95% confident precisions for typical aluminum anodizing solutions are 160.0 ± 1.9 g/l of sulfuric acid and 16.0 ± 0.8 g/l of oxalic acid, which are both an improvement by more than a factor of two over simple 95% confident precisions.

Keywords: Process monitoring; Statistical analysis; Sulfuric acid; Oxalic acid

1. Introduction

Inadequate monitoring of sulfuric and oxalic acids in anodizing solutions is a serious problem for the industry, resulting in poor quality products and wasted resources. These acid concentrations affect conductivity, solubility, wear resistance and oxide coating thickness, porosity and hardness. This is especially true for the narrow tolerances required to anodize armament systems. For anodizing solutions, the optimum operating ranges are 150 to 170 g/l of sulfuric acid and 11 to 21 g/l of oxalic acid. Current online and offline instrumental analysis methods either do not result in acceptable precisions or are time consuming [1–4]. A similar method, which is

an improvement on an existing ion chromatographic method, is presented here that provides acceptable analysis and monitoring of these acids in this anodizing process coupled with an extensive statistical evaluation of the experimental data.

2. Experimental

The following gives the details of the experimental procedures, materials and apparatus used. Strict analytical chemistry methods and procedures are followed throughout this experimental section [5].

A model 2020i Dionex ion chromatograph (Dionex, Sunnyvale, CA, USA) was used which

includes an autosampler, computer/ controller, computer/integrator and a suppressed conductivity detector [6].

A 5-ml sample was used for the autosampler. A 2.3 ml/min eluent flow-rate was used for the analytical pump. A 30 μS output range was used for the conductivity detector. The advanced chromatography module used a HPIC-AG4 separator column (Dionex), AMMS suppressor column (Dionex), a 5 ml/min regenerate flow-rate and a 10- μl injection loop. The conductivity detector was calibrated to 147 μS using 0.00100 *M* potassium chloride.

The initial scheduling conditions for the system computer/ controller module's equilibration (30 min), analysis (10 min each for alternating standards, S, and samples, A) and halt programs are one, eighteen and one iteration(s), respectively.

An analytical reagent grade solution is required for standard, S, containing 160 ± 1 g/l of sulfuric acid and 16.0 ± 1.0 g/l of oxalic acid. This standard solution is prepared and standardized using previous methods developed by this author [7–10]. Two other reagent-grade solutions are required: a 0.00095 *M* (0.100 ± 0.005 g/l) sodium carbonate eluent solution and a 0.0141 *M* (1.38 ± 0.04 g/l) sulfuric acid regenerate solution.

Preparation of an anodizing solution standard for ion chromatographic analysis requires that 1 ml of the analytical reagent grade standard solution (sulfuric and oxalic acid mixture) prepared above is diluted to the mark with deionized water in a 500-ml volumetric flask. Split sample solutions are prepared in the same manner. This 1:500 dilution coupled with the use of a 10- μl injection loop results in mean injection concentrations of 320 ppm sulfuric acid and 32.0 ppm oxalic acid.

Anodizing solution sample, A, is split into solutions A₁ and A₂. The anodizing solution standard, S, and samples A₁ and A₂ are placed in the autosampler in eighteen sealed 5 ml vials as follows: four of S for equilibration, three S/A₁ pairs for analysis, three S/A₂ pairs for analysis, an S and a deionized water.

A chromatograph is generated for each anodizing standard and sample solution, peak heights are determined, standard concentrations are known and sample concentrations and precisions are calculated using an extensive statistical method for reliability determinations.

3. Results and discussion

Statistical analysis is necessary to determine the reliability of the experimental ion chromatographic sample data in order to adequately monitor a given acid in the anodizing process.

There is significant dispersion in the ion chromatographic data relative to the narrow operating tolerances. This improved statistical analysis of the data splits an identical sample and takes three ion chromatographical measurements of each. A pooled T-test is calculated comparing the two sets of three measurements to see if they are statistically from the same sample. If they pass the T-test, then the validity of the results is significantly reinforced. If they fail the T-test, then the measurements are repeated until they pass this test. A number of references were used to support experimental design [11] and statistical analysis [12,13]. The comparison between the old and new method is that the old method did not reject results with respect to a tested dispersion threshold.

In the first of two parts of the statistical evaluation, a sample specimen is split, each split solution is analyzed in triplicate, and data from these split solutions are statistically compared. Fig. 1 shows a typical anodizing solution chromatograph with its large sulfuric acid peak and much smaller oxalic acid peak. The injection concentrations are large in order to maximize peak intensity. This optimization minimizes dispersion at the expense of slight column overload.

Table 1 gives the experimental mean peak height, X_3 , for each of the acid standards, S, and split sample solutions, A. The sample standard deviation S_{n-1} is

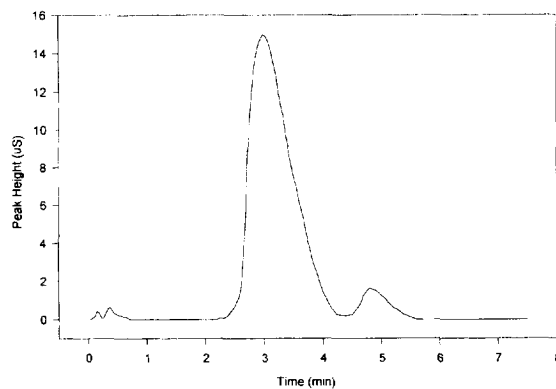


Fig. 1. Typical anodizing solution chromatograph.

Table 1
Peak height data for acids in typical anodizing solutions

	S_1	A_1	S_2	A_2
H_2SO_4				
$X_3(\mu S)$	15.73	14.98	15.73	14.85
$S_{n-1}(\mu S)$	± 0.26	± 0.20	± 0.13	± 0.23
$S_p(\mu S)$	–	± 0.23	–	± 0.19
$CL_{95\%}(g/l)$	–	± 5.57	–	± 4.64
$t_R(\text{min})$	2.99	2.99	2.99	2.99
$H_2C_2O_4$				
$X_3(\mu S)$	1.702	1.615	1.722	1.617
$S_{n-1}(\mu S)$	± 0.098	± 0.098	± 0.098	± 0.110
$S_p(\mu S)$	–	± 0.098	–	± 0.104
$CL_{95\%}(g/l)$	–	± 2.20	–	± 2.33
$t_R(\text{min})$	4.80	4.80	4.80	4.80

calculated for each of these samples and its associated standard. The pooled sample standard deviation S_p is calculated from the standard deviation of each sample and its associated standard as follows:

$$S_p = [(S_{n-1}^2 + S_{n-1}^2)/2]^{0.5} \quad (1)$$

In addition, the 95% percent confidence level, $CL_{95\%}$, in grams per liter is calculated from the above quantities for each sample and its associated standard

$$CL_{95\%} = (2.266)(S_p)[\text{acid std conc}/X_3] \quad (2)$$

Figs. 2 and 3 give typical sulfuric acid and oxalic acid calibration and 95% confidence data, respectively. The 95% confidence data in these figures agrees very well with the 95% confidence data calculated by Eq. 2 and given in Table 1.

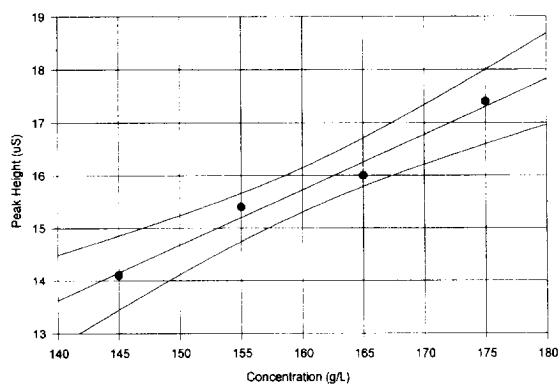


Fig. 2. Typical sulfuric acid calibration and 95% confidence data.

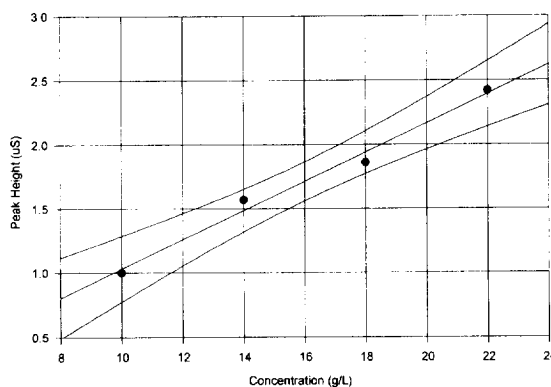


Fig. 3. Typical oxalic acid calibration and 95% confidence data.

Finally, the mean retention time (t_R) in minutes is given for each standard and split sample solution.

The concentration data of the split sample solutions are given in Table 2. As above, the mean X_3 , sample standard deviation S_{n-1} , and pooled sample standard deviation (S_p) are calculated. In addition, another quantity is calculated called the T -test value (T) for each sample solution from the following:

$$T = (1.225)[(X_3 - X_3)/S_p] \quad (3)$$

The experimental data of the split solutions of a sample solution are compared to a 2.776 value using the T -test to see if they are statistically from the same original sample solution to a 95% confidence level. A sample solution passes this T -test if its resultant absolute value is less than the 2.776 value. This T -test addresses the reliability dilemma mentioned above, since it either accepts or rejects a sample solution analysis. Samples solutions that fail the T -test are statistically dissimilar and are re-sampled and re-analyzed. Figs. 2 and 3 give typical dispersion data that is rejected by the T -test if dispersion exceeds the threshold tolerance.

Table 2
Concentration data for acids in typical anodizing solutions

	H_2SO_4 A_1	H_2SO_4 A_2	$H_2C_2O_4$ A_1	$H_2C_2O_4$ A_2
$X_3(g/l)$	152.4	151.0	15.20	15.02
$S_{n-1}(g/l)$	± 0.8	± 1.2	± 0.80	± 0.18
$S_p(g/l)$	–	± 1.0	–	± 0.58
T	–	1.7	–	0.38
$X_6(g/l)$	–	151.7	–	15.11
$S_n(g/l)$	–	± 1.2	–	± 0.53
$CL_{95\%p}(g/l)$	–	± 1.9	–	± 0.85

In the second part of the statistical evaluation, the mean, X_6 , and normal population standard deviation (S_n) are calculated for the six respective replicates of the sample solutions that have passed the T -test. Since this was the case, the concentration data for the unsplit and original sample solutions are also given in Table 2.

Previously, the variations in precision were examined for the materials, methods and instrumentation used. Clearly, the ion chromatographic system contributes the greatest amount of variation in precision compared to all other sources given for both anodizing acid constituents [10].

For the 20 g/l sulfuric acid operating tolerance band in these anodizing solutions, the 95% confident improved precision $CL_{95\%}$ (g/l) is about ± 1.9 g/l compared to the current ± 5.1 g/l value.

For the 10 g/l oxalic acid operating tolerance band in these anodizing solutions, the 95% confident improved precision $CL_{95\%}$ (g/l) is about ± 0.9 g/l compared to the current ± 2.3 g/l value.

The 95% confident precision bands in Figs. 2,3 collapse by more than a factor of two when this improved statistical method is used. For each acid, this improved statistical analysis that rejects/retests high dispersive data with respect to a tolerance threshold, allows more than twice as many precision bands to fit within its corresponding tolerance band. This improvement leads to a controllable armament anodizing system.

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