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# Utilization of ion chromatography and statistics to determine important acids in chromium plating and electropolishing solutions

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## Abstract

Inadequate monitoring of sulfuric and chromic acids in chromium plating solutions and phosphoric and sulfuric acids in electropolishing solutions is a serious problem for the industry resulting in poor quality products and wasted resources. This is especially true for the narrow tolerances required to chromium plate cannon systems. Current online and offline instrumental analysis methods either do not result in acceptable precision or are time consuming. Two similar methods, which are improvements on existing ion chromatographic methods, are presented here that provides acceptable analysis and monitoring of these acids in this chromium plating process coupled with an extensive statistical evaluation of the experimental data. For chromium plating solutions, the resultant means and precisions are  $2.50 \pm 0.11$  g/l sulfuric acid and  $250 \pm 5$  g/l chromic acid. For electropolishing solutions, these values are  $685 \pm 4$  g/l phosphoric acid and  $845 \pm 5$  g/l sulfuric acid.

## 1. Introduction

Inadequate monitoring of sulfuric and chromic acids in chromium plating solutions and phosphoric and sulfuric acids in electropolishing solutions is a serious problem for the industry resulting in poor quality products and wasted resources. This is especially true for the narrow tolerances required to chromium plate cannon systems. For chromium plating solutions, the optimum operating ranges are 2.40–3.10 g/l sulfuric acid and 230–270 g/l chromic acid. For electropolishing solutions, the optimum operating ranges are 640–730 g/l phosphoric acid and 795–895 g/l sulfuric acid. Current online and offline instrumental analysis methods, either do not result in acceptable precision or are time consuming [1–5]. Two similar methods, which are improvements on existing ion chromatographic methods, are presented here that provides acceptable analysis and monitoring of these acids in this chromium plating process coupled with an extensive statistical evaluation of the experimental data.

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## 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 [6].

A Model 2020i Dionex ion chromatograph (Dionex Corporation, Sunnyvale, CA, USA) was used which includes an autosampler, computer/controller, computer/integrator, and suppressed conductivity detector [7].

The initial conditions for the autosampler module are: local/remote is local, run/hold is hold then run, status is search, size is 5 ml, type is sample, inj is 1, tray is in/empty, type is loop, mode is prop, bleed is on, and inj/vial is 1.

The initial conditions for the analytical pump module are: local/remote is remote, start/stop is stop, flow is 2.3 ml/min, pressure limit select low alarm is 100 p.s.i. (1 p.s.i. = 6894.76 Pa), pressure limit select high alarm is 1000 p.s.i., and argon valve pressure is 100 p.s.i..

The initial conditions for the conductivity detector module are: local/remote is remote, cell is on, auto offset is off, temp. comp. is 0, and output range is 30  $\mu$ S.

The initial conditions for the advanced chromatography module are: load/inject is inject, valve A is off, valve B is off, local/remote is remote, separator column is HPIC-AG4 (Dionex), suppressor column is AMMS (Dionex), argon valve pressure is 100 p.s.i., regenerate flow is 5 ml/min, argon regenerate pressure is 6 p.s.i., and the injection loop is 10  $\mu$ l.

Fill the system reservoirs with the appropriate method eluent and regenerate. The analytical pump used for the eluent must be completely purged of air every time the eluent reservoir is filled. A properly functioning analytical pump is necessary for acceptable precision.

The conductivity detector should be periodically calibrated to 147  $\mu$ S using 0.00100 M potassium chloride.

The initial programming conditions for the system computer/controller module's equilibration program are: time is 0.0 min, load/inj is inject, valve B is on, offset is off, relays are off, and endrun is off. Conditions are the same at time is 30.0 min except endrun is on.

The initial programming conditions for the system computer/controller module's analysis program are: time is 0.0 min, load/inj is load, valve B is on, offset is off, relays are off, and endrun is off. Conditions are the same at time is 0.1 min except relays is £2. Conditions are the same at time is 0.2 min except relays are off. Conditions are the same at time is 2.2 min except offset is on. Conditions are the same at time is

2.3 min except load/inj is inject and relays is £1. Conditions are the same at time is 10.0 min except relays are off and endrun is on. Eluent flow rate is 2.3 ml/min., eluent port £3 is used, temp. select is zero, valve A is continually off, temp. comp. is 1.7, cond. setting full scale is 30  $\mu$ S, and AC outlets are all continually off.

The initial programming conditions for the system computer/controller module's halt program are: time is 0.0 min, load/inj is inject, valve B is off, offset is off, relays are off, and endrun is on. Eluent flow rate is 0.0 ml/min., no eluent port is selected, temp. select is zero, valve A is continually off, temp. comp. is zero, cond. setting full scale is 30  $\mu$ S, and AC outlets are all off.

The initial scheduling conditions for the system computer/controller module's equilibration, analysis, and halt programs are one, eighteen, and one iterations, respectively.

The initial programming conditions for the system computer/integrator are: AT = 1024, PH = 1, PT = 5000, and MN = 0.

The next three paragraphs outline the special conditions for the determination of chromic or sulfuric acid in chromium plating solutions.

Two analytical reagent grade standard solutions are required. The first is a  $2.95 \pm 0.01$  g/l sulfuric acid solution that meets American Chemical Society (ACS) and American Society For Testing Materials (ASTM) Standards [8,9]. The second is a  $250 \pm 1$  g/l chromic acid solution that meets ACS and Federal Standards [10,11]. E. M. Science reagent grade chromium trioxide is the only material found in our experience that meets ACS standards allowing a maximum of 0.005% sulfate. Two other reagent grade solutions are also required: a 0.00360 M ( $0.38 \pm 0.02$  g/l) sodium carbonate eluent solution and a 0.0141 M ( $1.38 \pm 0.04$  g/l) sulfuric acid regenerate solution.

Preparation of a chromium plating solution standard for ion chromatographic analysis requires that one ml of each of the analytical reagent grade standard solutions (sulfuric and chromic acids) prepared above are diluted to the mark with deionized water in a 250 ml volumetric flask. Split sample solutions are prepared

the same. This 1:250 dilution coupled with the use of a 10  $\mu$ l injection loop results in mean injection concentrations of 10 ppm sulfuric acid and 1000 mg/l chromic acid.

Only chromium plating solution sample 8 is run and is split into solutions 8-1 and 8-2. The chromium plating solution standard S and split samples 8-1 and 8-2 are placed in the autosampler in eighteen sealed 5 ml vials as follows: four S's, three S/8-1 pairs, three S/8-2 pairs, an S, and a deionized water.

The next three paragraphs outline the special conditions for the determination of sulfuric or phosphoric acid in electropolishing solutions.

One analytical reagent grade standard solution is required. It contains  $685 \pm 1$  g/l phosphoric acid and  $845 \pm 1$  g/l sulfuric acid. This standard solution is prepared and standardized using a previous method by this author [12]. Two other reagent grade solutions are required: a 0.00095 M ( $0.100 \pm 0.005$  g/l) sodium carbonate eluent solution and a 0.0141 M ( $1.38 \pm 0.04$  g/l) sulfuric acid regenerate solution.

Preparation of a electropolishing solution standard for ion chromatographic analysis requires that 0.400 ml of the analytical reagent grade standard solution (phosphoric and sulfuric acid mixture) prepared above is diluted to the mark with deionized water in a 2000 ml volumetric flask. Split sample solutions are prepared the same. This 1:5000 dilution coupled with the use of a 10  $\mu$ l injection loop results in mean injection

concentrations of 137 ppm phosphoric acid and 169 ppm sulfuric acid.

Only electropolishing solution sample 8P is run and is split into solutions 8P-1 and 8P-2. The electropolishing solution standard S and samples 8P-1 and 8P-2 are placed in the autosampler in eighteen sealed 5 ml vials as follows: four S's, three S/8P-1 pairs, three S/8P-2 pairs, an S, and a deionized water.

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

### 3. Results and discussion

A 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 chromium plating process. The statistical evaluation has two parts.

In the first part of the statistical evaluation, samples are split, each split solution is analyzed in triplicate, and data from these split solutions are statistically compared.

Tables 1–4 give the experimental peak height data for the acid standard and split sample solutions. For these Tables, raw peak height data

Table 1  
Ion chromatographic peak height data for sulfuric acid in chromium plating solutions

	Std S H <sub>2</sub> SO <sub>4</sub>	Samp 8-1 H <sub>2</sub> SO <sub>4</sub>	Std S H <sub>2</sub> SO <sub>4</sub>	Samp 8-2 H <sub>2</sub> SO <sub>4</sub>
Rep 1	170 185	163 899	173 776	163 668
Rep 2	176 065	165 987	169 989	163 303
Rep 3	173 267	159 973	170 932	161 416
$X_{avg}$	173 172	163 286	171 566	162 796
$S_{n-1}$	2941	3053	1971	1209
$S_p$	—	2998	—	1635
$C_{95\%}$ (g/l)	—	0.115	—	0.063
$t_R$ (min)	0.9	0.9	0.9	0.9

Peak heights expressed in IU.

Table 2  
Ion chromatographic peak height data for chromic acid in chromium plating solutions

	Std S CrO <sub>3</sub>	Samp 8-1 CrO <sub>3</sub>	Std S CrO <sub>3</sub>	Samp 8-2 CrO <sub>3</sub>
Rep 1	667 793	678 899	678 874	675 566
Rep 2	671 066	682 189	688 216	693 419
Rep 3	672 645	687 026	652 000	686 209
$X_{\text{avg}}$	670 501	682 704	673 030	685 064
$S_{n-1}$	2474	4087	18 801	8981
$S_p$	–	3378	–	14 733
$C_{95\%}$ (g/l)	–	2.9	–	12.4
$t_R$ (min)	1.9	1.9	1.9	1.9

Peak heights expressed in IU.

Table 3  
Ion chromatographic peak height data for phosphoric acid in electropolishing solutions

	Std S H <sub>3</sub> PO <sub>4</sub>	Samp 8P-1 H <sub>3</sub> PO <sub>4</sub>	Std S H <sub>3</sub> PO <sub>4</sub>	Samp 8P-2 H <sub>3</sub> PO <sub>4</sub>
Rep 1	562 500	509 200	573 900	512 700
Rep 2	572 000	507 700	575 800	516 100
Rep 3	573 300	509 100	578 700	517 100
$X_{\text{avg}}$	569 267	508 667	576 133	515 300
$S_{n-1}$	5896	839	2417	2307
$S_p$	–	4211	–	2363
$C_{95\%}$ (g/l)	–	11.5	–	6.4
$t_R$ (min)	1.8	1.8	1.8	1.8

Peak heights expressed in IU.

Table 4  
Ion chromatographic peak height data for sulfuric acid in electropolishing solutions

	Std S H <sub>2</sub> SO <sub>4</sub>	Samp 8P-1 H <sub>2</sub> SO <sub>4</sub>	Std S H <sub>2</sub> SO <sub>4</sub>	Samp 8P-2 H <sub>2</sub> SO <sub>4</sub>
Rep 1	813 800	770 200	815 700	762 300
Rep 2	821 400	764 600	813 600	763 200
Rep 3	819 500	763 000	810 400	760 500
$X_{\text{avg}}$	818 233	765 933	813 233	762 000
$S_{n-1}$	3955	3781	2669	1375
$S_p$	–	3869	–	2123
$C_{95\%}$ (g/l)	–	9.1	–	5.0
$t_R$ (min)	3.0	3.0	3.0	3.0

Peak heights expressed in IU.

is in integrator units (IC) and initially four equilibration standards are run before standard one. For Tables 1 and 2, standard solutions S and split sample solutions 8-1 and 8-2 are used after a 1:250 dilution. For Table 3 and 4, standard solutions S and split sample solutions 8P-1 and 8P-2 are used after a 1:5000 dilution.

For Tables 1-4, the mean  $X_{avg}$  and sample standard deviation  $S_{n-1}$  are 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:

$$S_p = [(S_1^2 + S_2^2)/2]^{0.5} \quad (1)$$

In addition, the ninety-five percent confidence level  $C_{95\%}$  in grams per liter is calculated from

the above quantities for each sample and its associated standard:

$$C_{95\%} = 2.266 \cdot S_p \cdot [\text{acid std conc}/\text{std } X_{avg}] \quad (2)$$

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 Tables 5 and 6. As above, the mean  $X_{avg}$ , 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:

$$T = 1.225 \cdot [(X_{1,avg} - X_{2,avg})/S_p] \quad (3)$$

The experimental data of the split solutions of

Table 5  
Concentration data for sulfuric and chromic acids in chromium plating solutions

	Samp 8-1 H <sub>2</sub> SO <sub>4</sub>	Samp 8-2 H <sub>2</sub> SO <sub>4</sub>	Samp 8-1 CrO <sub>3</sub>	Samp 8-2 CrO <sub>3</sub>
Rep 1	2.83	2.76	254	249
Rep 2	2.77	2.82	254	252
Rep 3	2.71	2.77	255	263
$X_{avg}$	2.77	2.78	254	255
$S_{n-1}$	0.060	0.032	0.577	7.37
$S_p$	—	0.048	—	5.22
$T$	—	0.254	—	0.234

Concentrations expressed in g/l.

Table 6  
Concentration data for phosphoric and sulfuric acids in electropolishing solutions

	Samp 8P-1 H <sub>3</sub> PO <sub>4</sub>	Samp 8P-2 H <sub>3</sub> PO <sub>4</sub>	Samp 8P-1 H <sub>2</sub> SO <sub>4</sub>	Samp 8P-2 H <sub>2</sub> SO <sub>4</sub>
Rep 1	620	612	800	790
Rep 2	608	614	787	793
Rep 3	608	612	787	793
$X_{avg}$	612	613	791	792
$S_{n-1}$	6.9	1.1	7.5	1.8
$S_p$	—	4.9	—	5.5
$T$	—	0.13	—	0.17

Concentrations expressed in g/l.

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.

In the second part of the statistical evaluation, the mean  $X_{\text{avg}}$  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 given in Table 7.

It is useful to evaluate the variations in precision for the materials and methods used. Volumes are calculated from the weight–volume relationship of the contained deionized water solution corrected for temperature. For ion chromatographic data, peak height is in integrator units (IU) and four equilibration replicates are run prior to data acquisition.

For chromium plating solutions, the six replicate experimental mean and precision of a Class A 1 ml micropipette is  $1.0102 \pm 0.0029$  ml [6]. The six replicate experimental mean and precision of a Class A 250 ml volumetric flask is

$249.49 \pm 0.03$  ml [6]. The six replicate experimental mean and precision of the titration of a 250 g/l chromic acid standard solution is  $250.2 \pm 0.2$  g/l [11]. The six replicate experimental mean and precision of the titration of a 2.95 g/l sulfuric acid standard solution is  $2.942 \pm 0.004$  g/l [9]. The six replicate peak height means and precisions of the ion chromatographic system determination of 2.95 g/l sulfuric acid and 250 g/l chromic acid standard solutions are given in Table 8. Six replicates by ion chromatography is equivalent to determining a split sample solution of 8.

For electropolishing solutions, the six replicate experimental mean and precision of a Class A 0.400 ml micropipette is  $0.400 \pm 0.002$  ml [6]. The six replicate experimental mean and precision of a Class A 2000 ml volumetric flask is  $2000 \pm 2$  ml [6]. The six replicate experimental mean and precision of the titration of a 685 g/l phosphoric acid standard solution is  $685 \pm 1$  g/l [12]. The six replicate experimental mean and precision of the titration of a 845 g/l sulfuric acid standard solution is  $845 \pm 1$  g/l [12]. The six replicate peak height means and precisions of the ion chromatographic system determination of 685 g/l phosphoric acid and 845 g/l sulfuric acid standard solutions are also given in Table 8. Six replicates by ion chromatography is equivalent to determining a split sample solution of 8P.

Clearly, the ion chromatographic system con-

Table 7  
Reported concentration data for chromium plating and electropolishing solutions

	Samp 8 H <sub>2</sub> SO <sub>4</sub>	Samp 8 CrO <sub>3</sub>	Samp 8P H <sub>3</sub> PO <sub>4</sub>	Samp 8P H <sub>2</sub> SO <sub>4</sub>
Rep 1	2.83	254	620	800
Rep 2	2.77	254	608	787
Rep 3	2.71	255	608	787
Rep 4	2.76	249	612	790
Rep 5	2.82	252	614	793
Rep 6	2.77	263	612	793
$X_{\text{avg}}$	2.77	254	612	792
$S_n$	0.04	4	4.0	4.5

Concentrations expressed in g/l.

Table 8

Ion chromatographic peak height precisions of chromium plating process standard acid solutions

	Samp 8 H <sub>2</sub> SO <sub>4</sub>	Samp 8 CrO <sub>3</sub>	Samp 8P H <sub>3</sub> PO <sub>4</sub>	Samp 8P H <sub>2</sub> SO <sub>4</sub>
Rep 1	189 500	699 600	562 500	813 800
Rep 2	185 300	697 000	572 000	821 400
Rep 3	186 900	677 700	573 300	819 500
Rep 4	182 000	663 800	573 900	815 700
Rep 5	187 800	705 000	575 800	813 600
Rep 6	183 900	680 800	578 700	810 400
$X_{avg}$	185 900	687 317	572 700	815 700
$S_n$	2725	15 782	5032	3720

Peak heights expressed in IU.

tributes the greatest amount of variation in precision compared to all other sources given for both of the above methods.

For chromium plating solutions, the resulting precisions are in the range of 0.03–0.20 g/l sulfuric acid and 1–9 g/l chromic acid. For electropolishing solutions, the resulting precision are in the range of 2–7 g/l phosphoric acid and 2–8 g/l sulfuric acid. The data shows that these improved methods are sufficient to monitor these acids in the chromium plating process.

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