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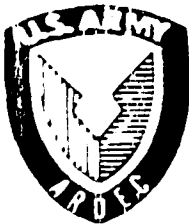
TECHNICAL REPORT ARCCB-TR-88026

**DETERMINATION OF SULFURIC ACID, OXALIC
ACID, AND THEIR MATRIX EFFECTS IN ALUMINUM
ANODIZING SOLUTIONS BY ION CHROMATOGRAPHY**

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Process optimization of aluminum anodizing and hardcoating solutions requires determinations of sulfuric and oxalic acids. An improved ion chromatographic procedure is given for standards and samples of these analytes addressing matrix effects caused by dissimilar acid-base characteristics and concentrations.		

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INTRODUCTION

Anodizing and hardcoating (hard anodizing) of aluminum improve corrosion and wear resistance. Acid concentrations (sulfuric, oxalic), pH, and physical plating variables (current, temperature, time) affect oxide coating thickness, porousness, hardness, solubility, and conductivity. Hardcoating solutions typically contain 120-160 g/l sulfuric acid (H_2SO_4) and 12-21 g/l oxalic acid ($H_2C_2O_4$), while anodizing solutions typically contain 160-200 g/l H_2SO_4 . Lower acid concentration hardcoating solutions give oxide coatings that are thicker, harder, less porous, less soluble, and more wear resistant compared to higher acid concentration anodizing solutions. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) are commonly used to adjust the pH of these metal finishing solutions (ref 1).

The acids and sodium salts of sulfate and oxalate have been determined in a variety of matrices (refs 2-4), although not for anodizing and hardcoating solutions. A reference standard for instrumental analysis of sulfate or oxalate ions is commonly made from either the acids or the sodium salts. Anodizing and hardcoating sample solution acids and sodium salts are present for these analytes and cause matrix effects when compared to the reference standards. These matrix effects may produce considerable variation in the commonly used analytical response of peak height, and result from dissimilar samples and standards affecting the eluent and separator column differently. An improved chromatographic procedure that addresses these matrix effects is given for anodizing and hardcoating solutions.

References are listed at the end of this report.

EXPERIMENTAL PROCEDURE

All the components of the analytical system are from Dionex Corporation (Sunnyvale, CA) using their model 2020i ion chromatograph. The system flowstream consists of the eluent reservoir (0.001 M sodium carbonate), eluent delivery system (2.3 ml/min), injector valve (10 μ l loop), separator column (HPIC-AG4), chemical suppressor (2.1 ml/min, 0.015 M H₂SO₄), and conductivity detector (30 μ SFS). The integrator attenuation is 1024.

The standard reference stock solution consists of 150 g/l H₂SO₄ and 18.0 g/l H₂C₂O₄ with no HCl or NaOH present. Other stock solutions were prepared that varied from no HCl to 0.1N HCl and from no NaOH to 0.1N NaOH while maintaining the H₂C₂O₄ concentrations of the standard reference stock solution. In addition, standard stock solutions were prepared that have 0.1 and 1.5 times the H₂SO₄ and H₂C₂O₄ concentrations of the standard reference stock solution. Finally, standard stock solutions were prepared for the equivalent sulfate and oxalate concentrations as above using the sodium salt. All standard stock solutions of anodizing and hardcoating solutions require a 500 dilution before injection.

RESULTS AND DISCUSSION

Table I shows how variations of acid-base characteristics for solutions of sulfate and oxalate ions affect their peak heights and retention times. Data in this table are with respect to the reference solution which contains no added acid or base. Solutions containing acid or base have apparent concentrations that deviate significantly from the actual reference solution values.

Addition of HCl or NaOH to the reference solution prior to eluent injection causes an equivalent amount of acid-base association or dissociation with

respect to bisulfate and bioxalate. Injection of solutions with varied acid-base characteristics overwhelms the carbonate-bicarbonate buffered eluent equilibrium in a proportion equal to the added acid or base. A change of eluent pH by one unit due to added acid or base will change the carbonate-bicarbonate ionic ratio of 3:1 by a factor of ten. Since carbonate is a much stronger pushing ion compared to bicarbonate, the altered ratio values significantly alter eluent strength with a profound effect on retention times, band broadening, and tailing of analyte peaks. The momentary presence of bisulfate or bioxalate will reduce peak tailing due to ion exchange resin affinity of these ions. Dissociation constants support the acid-base variation that occurs at the pH values involved. Addition of HCl has more of a downward effect on the sample and eluent pH than the upward effect of added NaOH due to the moderately basic eluent.

Addition of any high concentration anions with low ion exchange resin affinities such as chloride or hydroxide will supplement the pushing action of the eluent for the higher affinity analytes and reduce the retention times. These changes in analyte and eluent ions affect retention times, peak heights, and peak shapes, and are significant to the analytical response.

If the equivalent amount of sulfate and oxalate as their sodium salts instead of their acid forms is used as in the reference solution, it would be the same as neutralizing these acids in the reference solution with NaOH. The results of this solution lie near 0.10N NaOH in Table I as expected.

Table II shows that variations in analyte sample concentrations also vary retention times resulting in non-linear calibration curves with respect to peak height. As in Table I, column loading concentrations, eluent changes, and

analyte changes affect the analytical response. The middle concentration for each analyte in Table II is the standard reference solution.

For the reference solution, the addition of acid or base, or a wide variation in analyte concentrations can significantly affect the analytical response. Variations in sample dilutions do not resolve these differences in response.

The results show the necessity for utilizing standards and samples of similar acid-base characteristics and analyte concentrations accomplished by preparation from similar compounds. If standards and samples have dissimilar acid-base characteristics, then it is necessary to adjust both to a common pH value using an appropriate acid or base to achieve quantitative analysis.

Four years of testing have provided analyte ion variations, including accuracy and precision of about three percent.

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TABLE I. CHROMATOGRAPHIC RESULTS OF ACID-BASE VARIATIONS
FOR ANODIZING SOLUTIONS

HCl/NaOH(N)	H ₂ SO ₄			H ₂ C ₂ O ₄		
	RT(min)	H(μS)	Apparent Conc(g/l)	RT(min)	H(μS)	Apparent Conc(g/l)
0.100/0.000	3.7	24.8	145	-	-	-
0.010/0.000	3.7	25.2	147	4.9	1.67	17.9
0.001/0.000	3.6	25.5	149	4.9	1.67	17.9
0.000/0.000	3.6	25.7	150	4.9	1.68	18.0
0.000/0.001	3.6	25.7	150	4.8	1.69	18.1
0.000/0.010	3.5	25.8	151	4.8	1.70	18.2
0.000/0.100	3.4	26.0	152	4.6	1.74	18.6

TABLE II. CHROMATOGRAPHIC RESULTS OF CONCENTRATION VARIATIONS
FOR ANODIZING SOLUTIONS

Analyte	Actual Conc (g/l)	RT(min)	H(μ S)	Apparent Conc (g/l)
H ₂ SO ₄	75	3.9	16.1	94
H ₂ SO ₄	150	3.6	25.7	150
H ₂ SO ₄	225	3.5	33.9	198
H ₂ C ₂ O ₄	9.0	5.1	0.97	10.4
H ₂ C ₂ O ₄	18.0	4.9	1.68	18.0
H ₂ C ₂ O ₄	27.0	4.8	2.35	25.2

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