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TECHNICAL REPORT ARCCB-TR-88025

**DETERMINATION OF PHOSPHORIC ACID,
SULFURIC ACID, CHROMIC ACID, AND THEIR
MATRIX EFFECTS IN CHROMIUM PLATING
AND ASSOCIATED POLISHING SOLUTIONS
BY ION CHROMATOGRAPHY**

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SAMUEL SOPOK

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**US ARMY ARMAMENT RESEARCH,
DEVELOPMENT AND ENGINEERING CENTER
CLOSE COMBAT ARMAMENTS CENTER
BENÉT LABORATORIES
WATERVLIET, N.Y. 12189-4050**



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20. ABSTRACT (CONT'D)

these determinations. Established precisions and sensitivities did not vary in this new procedure.

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INTRODUCTION

Historical (ref 1), specific (refs 2-8), and general (refs 9-11) references are given for the determination of phosphoric, sulfuric, and chromic acids (H_3PO_4 , H_2SO_4 , and CrO_3 , respectively) by ion chromatography. These references contain established procedures for a variety of solution matrices where the actual analytes determined are phosphate, sulfate, and chromate ions. For all past work, standards and samples of these analytes are either made totally from their acid or sodium salt. All acid-base and concentration characteristics are well known and no mixtures of acids and sodium salts are used. Many real-life samples do not have well-known characteristics and contain mixtures of acids and salts of analytes and non-analytes. This is commonly the case for chromium plating, polishing, and their associated waste solutions. There is up to a forty percent variation in the commonly used analytical response of peak height for solutions with the same analyte concentrations due to the use of acids or sodium salts to make solutions. Analytical response variation is due to dissimilar samples and standards affecting the eluent and separator column differently. Practical procedural modifications for analyzing these unknown samples are addressed.

EXPERIMENTAL PROCEDURE

The analytical system used is the Dionex 2020i ion chromatograph. The system flowstream consists of the eluent reservoir (0.003 M sodium carbonate for plating and 0.001 M sodium carbonate for polishing solutions), eluent delivery system (2.3 ml/min), injector valve (10 μ l loop), separator column (Dionex HPIC-AG4), UV-visible detector (Dionex, 440 nm, 0.01 AUFS), chemical suppressor

References are listed at the end of this report.

(2.1 ml/min, 0.015 M H₂SO₄), conductivity detector (Dionex, 30 μSFS), and an atomic absorption detector (Perkin-Elmer, 357.9 nm, aspirator flow rate is 2.8 ml/min). Airtight coupling of the atomic absorption detector is accomplished with standard tubing provided.

Matrix types include chromium plating (2.50 g/l H₂SO₄, 250 g/l CrO₃, and 0.50 g/l H₃PO₄) and polishing (680 g/l H₃PO₄, 840 g/l H₂SO₄, and 1.00 g/l CrO₃) solutions at typical operating concentrations. The standard analyte reference solution has no hydrochloric acid (HCl) or sodium hydroxide (NaOH) for each matrix type. Also for each matrix type, standard stock solutions were prepared that varied from no HCl to 0.1 N HCl and from no NaOH to 0.1 N NaOH, while maintaining the initial constant reference matrix. In addition, for each matrix type, standard stock solutions were prepared that have 0.5 and 1.5 times the initial matrix concentrations. Finally for each matrix type, standard stock solutions were prepared for the equivalent analyte concentration, but using the sodium salt. All standard stock solutions and samples require a 250 dilution for chromium plating solutions and a 2500 dilution for polishing solutions prior to injection in order to attain detector linearity.

The integrator (Dionex) attenuation values are 1024, 1024, and 256 for the conductivity, UV-visible, and atomic absorption detectors, respectively.

RESULTS AND DISCUSSION

The variation of acid-base characteristics for a solution of sulfate, chromate, and phosphate ions affects their peak height and retention times as shown in Tables I and II. Some analyte peaks are lost in the large chloride peak or hydroxide dips as shown. In general, the peak area is unaffected. All data in these tables 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, dichromate, and biphosphate for these analyte ions. Injection of solutions with varied acid-base characteristics overwhelms the carbonate-bicarbonate buffered eluent equilibrium in proportion to the amount of acid or base added. If the eluent pH is increased due to added base or decreased due to added acid from its pH = 11 (approximate) value by one pH unit, then the carbonate-bicarbonate ionic ratio of 3:1 will increase or decrease by a factor of ten, respectively. Since carbonate is a much stronger pushing ion than 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 and biphosphate will reduce peak tailing, while the momentary presence of dichromate will increase 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 pH = 11 (approximate) value of the 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 their 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 chromate as sodium chromate instead of chromic acid is used as in the reference solution, then that would be the same as neutralizing the chromic acid in the reference solution with 0.014 N NaOH, including the minimal H_2SO_4 effect. The results of this solution lie near 0.01 N NaOH in Table I as expected. This exercise is true for all analytes.

Tables III and IV show that variations in analyte sample concentrations will also vary retention times resulting in non-linear calibration curves with respect to peak height. Again, peak areas are unaffected. As in Tables I and II, column loading concentrations, eluent changes, and analyte changes affect the analytical response. The middle concentration for each analyte is that of the standard reference solution in Tables III and IV.

For Tables I and III, UV-visible and atomic absorption detection support the results of conductivity detection that this variation is independent of the detector for chromate and is due to sample-eluent-column interactions.

For the reference solution, the addition of more than 0.001 N acid or base, or a wide variation in analyte concentrations can significantly affect the analytical response and variations in sample dilutions do not resolve these differences in response.

These results show the necessity for utilizing standards and samples of similar acid-base characteristics and analyte concentrations when these solutions are analyzed by ion chromatography. Preparation from similar compounds will accomplish this. 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 before analysis to achieve quantitative results.

Four years of testing have provided major and trace analyte ion variations (accuracy and precision) of about two and four percent, respectively.

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

HCl/NaOH(N)	Sulfate			Chromate		
	RT(min)	H(μ S)	Apparent Conc. (g/l)	RT(min)	H(μ S)	Apparent Conc. (g/l)
0.100/0	-	-	-	2.7	5.26	149
0.010/0	-	-	-	2.2	6.36	180
0.001/0	0.92	1.02	2.16	2.0	8.78	249
0/0	0.92	1.18	2.50	2.0	8.82	250
0/0.001	0.92	1.18	2.50	2.0	8.80	249
0/0.010	0.92	1.18	2.50	1.9	9.63	273
0/0.100	0.92	1.17	2.48	1.8	11.5	326

TABLE II. CHROMATOGRAPHIC RESULTS OF ACID-BASE VARIATIONS
FOR POLISHING SOLUTIONS

HCl/NaOH(N)	Phosphate			Sulfate		
	RT(min)	H(μ S)	Apparent Conc.(g/l)	RT(min)	H(μ S)	Apparent Conc.(g/l)
0.100/0	-	-	-	3.1	15.7	835
0.010/C	1.8	10.3	673	3.0	15.8	840
0.001/0	1.8	10.4	680	3.0	15.8	840
0/0	1.8	10.4	680	3.0	15.8	840
0/0.001	1.8	10.4	680	3.0	15.4	819
0/0.010	1.7	10.6	693	2.9	15.3	813
0/0.100	1.7	10.8	706	2.8	15.2	808

TABLE III. CHROMATOGRAPHIC RESULTS OF CONCENTRATION VARIATIONS
FOR CHROMIUM PLATING SOLUTIONS

Analyte	Actual Conc. (g/l)	RT(min)	H(μ S)	Apparent Conc. (g/l)
H ₂ SO ₄	1.25	0.95	0.63	1.33
H ₂ SO ₄	2.50	0.92	1.18	2.50
H ₂ SO ₄	3.75	0.91	1.70	3.60
CrO ₃	125	2.3	5.06	143
CrO ₃	250	2.0	8.82	250
CrO ₃	375	1.7	12.4	351

TABLE IV. CHROMATOGRAPHIC RESULTS OF CONCENTRATION VARIATIONS
FOR POLISHING SOLUTIONS

Analyte	Actual Conc. (g/l)	RT(min)	H(μ S)	Apparent Conc. (g/l)
H ₃ PO ₄	340	1.9	5.54	362
H ₃ PO ₄	680	1.7	10.4	680
H ₃ PO ₄	1020	1.6	14.0	915
H ₂ SO ₄	420	3.3	10.1	537
H ₂ SO ₄	840	3.0	15.8	840
H ₂ SO ₄	1260	2.9	20.1	1069

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