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# X-RAY FLUORESCENCE ON-STREAM ANALYSIS OF STANDARD REFERENCE SOLUTION CONCENTRATIONS OF CHROMIUM PLATING AND POLISHING SOLUTIONS

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# X-Ray Fluorescence On-Stream Analysis of Standard Reference Solution Concentrations of Chromium Plating and Polishing Solutions

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## Abstract

X-ray fluorescence is evaluated as a means to quantitatively analyze standard reference solution concentrations of chromium plating and polishing solutions for chromium, sulfur, phosphorus, and iron in a continuous, on-stream fashion. The identical experiment was conducted at two different manufacturers of this type of instrument and included calibration/standardization with standard reference chromium plating and polishing solutions, analysis with coded standard reference chromium plating and polishing solutions, calibration/standardization with standard reference chromium plating and polishing wastewater solutions, and analysis with coded standard reference chromium plating and polishing wastewater solutions. Resultant data and their corresponding precisions show promise for this application and may complement current off-stream laboratory methods now in use. More work will be conducted to further determine the value of this technique.

## Keywords

Chemical analysis, chromium plating solutions, polishing solutions, x-ray fluorescence on-stream analysis.

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## Introduction

Current analytical methods now in use to determine chromium plating and polishing solution analytes are appropriate only for a laboratory environment (1-6). On-stream monitoring for the analyte concentrations of chromium plating and polishing solutions may complement present analytical methods and provide valuable production data. Recent work using x-ray fluorescence on-stream analysis to determine analyte concentrations of chromium plating solutions (7-9) appears to address part of the goal of on-stream monitoring discussed above at least for chromium plating solutions. This report evaluates the use of x-ray fluorescence on-stream analysis of standard reference solution concentrations of chromium plating and polishing solutions in relation to the stated goals.

## Approach

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (10).

Many analytical reagent grade standard reference and coded standard reference solutions are required. These solutions are prepared to completely cover the operating ranges of normal production type chromium plating and polishing analyte concentrations in these solutions. Tables 1 - 2 give these chromium plating and polishing solutions and their analyte concentrations. The six references by Sopok (1-6) provide extensive information for preparing and chemically analyzing these standard reference solutions for all analytes listed in Tables 1 - 2. These analytical chemistry methods (1-6) are used for quality control purposes for these standard reference solutions.

The general analytical system used is an on-stream x-ray fluorescence spectrometer (approximate cost: $70,000) that provides continuous elemental (chromium, sulfur, phosphorus, and iron) analyses of these solutions. Identical experiments were conducted on this type of instrumentation by Asoma Instruments Corp. (Austin, Texas) and Tracor X-ray Corp. (Mountain View, Calif.). Each company publishes manuals that are an excellent source of reference for operating conditions, operation, and maintenance of these instruments (11-12). All solutions are analyzed in triplicate and no dilutions are required. These experiments were conducted in a blind fashion due to the use of coded standard reference solutions.

The experimental approach included calibration/standardization with standard reference chromium plating and polishing solutions, analysis with coded standard reference chromium

plating and polishing solutions, calibration/standardization with standard reference chromium plating and polishing wastewater solutions, and analysis with coded standard reference chromium plating and polishing wastewater solutions. Uncoded calibration/standardization solution data were used to determine analyte concentrations of coded solution data.

## Results and Discussion

Experimental Asoma and Tracor calibration/standardization data are given in Tables 3 - 8 for standard reference chromium plating and polishing solutions.

Experimental Asoma and Tracor analysis data are given in Tables 9 - 16 for coded standard reference chromium plating and polishing solutions. All experimental analysis data given in Tables 9 - 16 are coded and comprised of randomly duplicated solutions. Data given in Tables 17 - 22 show that the duplicate solutions in Tables 9 - 16 are statistically the same except in one case. The method used to determine this statistical evaluation involves a variation of the standard Student t-test and is extensively discussed elsewhere for an experiment with identical characteristics (3).

Experimental Asoma and Tracor calibration/standardization and analysis data are given in Tables 23 - 24 for standard reference chromium plating and polishing wastewater solutions. These two tables show experimental wastewater detection limits for chromium, sulfur, phosphorus, and iron in these chromium plating and polishing solutions.

An advantage of this experiment is that the standard reference chromium plating and polishing solutions covered the entire operational concentration ranges for each analyte thus optimizing calibration, standardization, and analysis. Another experimental advantage is that the analyte concentrations of these solutions were well-known since they were carefully prepared from analytical reagent materials. Finally, these analyte solution concentrations were verified by presently-used laboratory chemical analysis methods (1-6) for quality assurance purposes.

A disadvantage of this experiment is that only the solution analytes sought in these standard reference solutions varied, while the unsought solution analytes remained constant with respect to concentration that may provide better than normal data and precision. Another experimental disadvantage is that these standard reference solutions were never used for plating or polishing and, as a result, this experiment ignores the possible analysis effects of non-analyte chemical or particulate contaminates resulting from these processes.

An observation of this experiment is that each company had limited experience with chromium plating and polishing solution analysis, although the final methods developed were similar.

This experiment provides elemental analysis of chromium and does not distinguish between trivalent and hexavalent chromium. A second on-stream instrument (Spectronic-20 uv-visible spectrophotometer, on-stream mode, estimated cost $1,000, Bausch and Lomb) separately provides a direct trivalent chromium analysis without dilution using a very small pathlength cell. Then the hexavalent chromium solution concentration is calculated by the difference between the x-ray fluorescence and uv-visible analysis methods.

The x-ray fluorescence chemical analysis method is non-destructive, applicable to multiple process streams, and requires no dilutions for these chromium plating and polishing solutions. In addition, monthly calibration, standardization, and maintenance are required for proper instrument use.

A second experiment is planned to further evaluate on-stream x-ray fluorescence for chromium plating and polishing solutions. This experiment will be conducted using actual chromium plating and polishing solutions. Elemental concentration ranges and their intervals will be simultaneously randomized to the extent possible, although the elemental operating ranges will be covered. A primary concern of this experiment is the possible analysis effects of non-analyte chemical or particulate contaminates resulting from normal chromium plating and polishing solutions.

Resultant data and their corresponding precisions show promise for this application and may complement current off-stream laboratory methods now in use. More work will be conducted to further determine the value of this technique.

**Table 1. Chromium Plating Standard Solutions**

| Uncoded Standards | $CrO_3$ Values (Actual) | $H_2SO_4$ Values (Actual) | Fe Values (Actual) |
|---|---|---|---|
| A —> E | 240 - 260 | 2.70 | 3.75 |
| F —> J | 250 | 2.50 - 2.90 | 3.75 |
| K —> O | 250 | 2.70 | 0 - 7.50 |

| Coded Standards | $CrO_3$ Values (Actual) | $H_2SO_4$ Values (Actual) | Fe Values (Actual) |
|---|---|---|---|
| W | 245 | 2.60 | 1.88 |
| X | 245 | 2.60 | 1.88 |
| Y | 255 | 2.80 | 5.63 |
| Z | 255 | 2.80 | 5.63 |

All units are in grams/liter; wastewater detection limits were determined for each element between 10 —> 1000 ppm concentration.

**Table 2. Polishing Standard Solutions**

| Uncoded Standards | $H_3PO_4$ Values (Actual) | $H_2SO_4$ Values (Actual) | Fe Values (Actual) |
|---|---|---|---|
| 1 —> 5 | 640 - 720 | 840 | 7.50 |
| 6 —> 10 | 680 | 795 - 885 | 7.50 |
| 11 —> 15 | 680 | 840 | 0 - 15.00 |

| Coded Standards | $H_3PO_4$ Values (Actual) | $H_2SO_4$ Values (Actual) | Fe Values (Actual) |
|---|---|---|---|
| 96 | 660 | 818 | 3.75 |
| 97 | 660 | 818 | 3.75 |
| 98 | 700 | 863 | 11.25 |
| 99 | 700 | 863 | 11.25 |

All units are in grams/liter; wastewater detection limits were determined for each element between 10 —> 1000 ppm concentration.

**Table 3. $CrO_3$ in Chromium Plating Solutions - Experimental Calibration/Standardization Data**

| $CrO_3$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 240.0 | 239.3 | 241.0 | 0.6 | 4.4 |
| 245.0 | 244.7 | 244.6 | 0.6 | 3.5 |
| 250.0 | 249.7 | 246.3 | 0.6 | 0.6 |
| 255.0 | 254.7 | 255.3 | 0.6 | 3.5 |
| 260.0 | 259.0 | 260.3 | 0.0 | 2.9 |

All units are in grams/liter; all solutions contain 2.70 g/l $H_2SO_4$ and 3.75 g/l Fe.

**Table 4. $H_2SO_4$ in Chromium Plating Solutions-Experimental Calibration/Standardization Data**

| $H_2SO_4$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 2.50 | 2.45 | 2.46 | 0.07 | 0.19 |
| 2.60 | 2.58 | 2.55 | 0.11 | 0.20 |
| 2.70 | 2.70 | 2.59 | 0.11 | 0.11 |
| 2.80 | 2.76 | 2.88 | 0.11 | 0.07 |
| 2.90 | 2.95 | 2.86 | 0.08 | 0.14 |

All units are in grams/liter; all solutions contain 250 g/l $CrO_3$ and 3.75 g/l Fe; chloride is an interference.

**Table 5. Fe in Chromium Plating Solutions - Experimental Calibration/Standardization Data**

| Fe Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 0.00 | 0.05 | 0.00 | 0.23 | 0.19 |
| 1.88 | 1.67 | 1.91 | 0.20 | 0.12 |
| 3.75 | 3.85 | 3.85 | 0.22 | 0.07 |
| 5.63 | 5.62 | 5.54 | 0.18 | 0.04 |
| 7.50 | 7.20 | 7.52 | 0.28 | 0.05 |

All units are in grams/liter; all solutions contain 250 g/l $CrO_3$ and 2.70 g/l $H_2SO_4$.

**Table 6. $H_3PO_4$ in Polishing Solutions - Experimental Calibration/Standardization Data**

| $H_3PO_4$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 640.0 | 640.6 | 643.0 | 0.6 | 5.6 |
| 660.0 | 660.0 | 657.0 | 0.0 | 7.2 |
| 680.0 | 680.7 | 683.7 | 1.2 | 7.2 |
| 700.0 | 700.3 | 702.7 | 0.6 | 7.4 |
| 720.0 | 720.0 | 719.7 | 1.0 | 6.7 |

All units are in grams/liter; all solutions contain 840 g/l $H_2SO_4$ and 7.50 g/l Fe.

**Table 7. $H_2SO_4$ in Polishing Solutions - Experimental Calibration/Standardization Data**

| $H_2SO_4$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 795.0 | 795.3 | 800.3 | 1.2 | 19.5 |
| 818.0 | 817.0 | 827.3 | 1.0 | 8.5 |
| 840.0 | 840.3 | 851.0 | 0.6 | 5.6 |
| 863.0 | 862.7 | 870.3 | 1.2 | 10.3 |
| 885.0 | 884.7 | 892.7 | 1.5 | 6.8 |

All units are in grams/liter; all solutions contain 680 g/l $H_3PO_4$ and 7.50 g/l Fe.

**Table 8. Fe in Polishing Solutions - Experimental Calibration/Standardization Data**

| Fe Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 0.00 | 0.19 | 0.05 | 0.29 | 0.05 |
| 3.75 | 3.76 | 3.66 | 0.27 | 0.05 |
| 7.50 | 7.36 | 7.45 | 0.22 | 0.04 |
| 11.25 | 11.20 | 11.29 | 0.31 | 0.08 |
| 15.00 | 14.94 | 14.95 | 0.28 | 0.05 |

All units are in grams/liter; all solutions contain 680 g/l $H_3PO_4$ and 840 g/l $H_2SO_4$.

**Table 9. Chromium Plating Solutions - Experimental Analysis Data**

| Sample Pair (Actual) | $CrO_3$ Value (Actual) | $H_2SO_4$ Value (Actual) | Fe Value (Actual) |
|---|---|---|---|
| W & X | 245 | 2.60 | 1.88 |
| Y & Z | 255 | 2.80 | 5.63 |

All units are in grams/liter; all elements in each solution pair passed t-test for both Asoma and Tracor.

**Table 10. $CrO_3$ in Chromium Plating Solutions - Experimental Analysis Data**

| $CrO_3$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 245.0 | 245.0 | 246.3 | 0.0 | 2.1 |
| 245.0 | 245.7 | 245.0 | 0.6 | 3.6 |
| 255.0 | 255.7 | 256.7 | 0.6 | 2.1 |
| 255.0 | 255.7 | 256.7 | 0.6 | 3.2 |

All units are in grams/liter; 1st and 2nd solutions contain 2.60 g/l $H_2SO_4$ and 1.88 g/l Fe; 3rd and 4th solutions contain 2.80 g/l $H_2SO_4$ and 5.63 g/l Fe.

**Table 11. $H_2SO_4$ in Chromium Plating Solutions - Experimental Analysis Data**

| $H_2SO_4$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 2.60 | 2.59 | 2.68 | 0.09 | 0.06 |
| 2.60 | 2.58 | 2.62 | 0.08 | 0.15 |
| 2.80 | 2.80 | 2.72 | 0.08 | 0.19 |
| 2.80 | 2.77 | 2.76 | 0.11 | 0.15 |

All units are in grams/liter; 1st and 2nd solutions contain 245 g/l $CrO_3$ and 1.88 g/l Fe; 3rd and 4th solutions contain 255 g/l $CrO_3$ and 5.63 g/l Fe.

**Table 12. Fe in Chromium Plating Solutions - Experimental Analysis Data**

| Fe Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 1.88 | 1.88 | 1.84 | 0.19 | 0.08 |
| 1.88 | 1.95 | 1.78 | 0.30 | 0.02 |
| 5.63 | 5.58 | 5.54 | 0.26 | 0.06 |
| 5.63 | 5.56 | 5.63 | 0.31 | 0.11 |

All units are in grams/liter; 1st and 2nd solutions contain 245 g/l $CrO_3$ and 2.60 g/l $H_2SO_4$; 3rd and 4th solutions contain 255 g/l $CrO_3$ and 2.80 g/l $H_2SO_4$.

**Table 13. Polishing Solutions - Experimental Analysis Data**

| Sample Pair (Actual) | $H_3PO_4$ Value (Benét) | $H_2SO_4$ Value (Benét) | Fe Value (Benét) |
|---|---|---|---|
| 96 & 97 | 660 | 818 | 3.75 |
| 98 & 99 | 700 | 863 | 11.25 |

All units are in grams/liter; all elements in each solution pair passed t-test for both Asoma and Tracor.

**Table 14. $H_3PO_4$ in Polishing Solutions - Experimental Analysis Data**

| $H_3PO_4$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 660.0 | 658.7 | 658.0 | 0.6 | 7.9 |
| 660.0 | 660.7 | 661.3 | 0.6 | 7.0 |
| 700.0 | 700.3 | 698.7 | 0.6 | 5.5 |
| 700.0 | 700.0 | 702.3 | 1.7 | 3.2 |

All units are in grams/liter; 1st and 2nd solutions contain 818 g/l $H_2SO_4$ and 3.75 g/l Fe; 3rd and 4th solutions contain 863 g/l $H_2SO_4$ and 11.25 g/l Fe.

**Table 15. $H_2SO_4$ in Polishing Solutions - Experimental Analysis Data**

| $H_2SO_4$ Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 818.0 | 817.7 | 812.3 | 0.6 | 5.7 |
| 818.0 | 817.7 | 822.3 | 1.2 | 5.5 |
| 863.0 | 862.7 | 858.0 | 1.5 | 9.5 |
| 863.0 | 862.3 | 857.0 | 0.6 | 4.4 |

All units are in grams/liter; 1st and 2nd solutions contain 660 g/l $H_3PO_4$ and 3.75 g/l Fe; 3rd and 4th solutions contain 700 g/l $H_3PO_4$ and 11.25 g/l Fe.

**Table 16. Fe in Polishing Solutions - Experimental Analysis Data**

| Fe Values (Actual) | Exp. Mean (n=3) | | Exp. s.d. (n=3) | |
|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor |
| 3.75 | 3.85 | 3.82 | 0.23 | 0.05 |
| 3.75 | 3.64 | 3.76 | 0.30 | 0.05 |
| 11.25 | 11.22 | 11.19 | 0.26 | 0.04 |
| 11.25 | 11.15 | 11.21 | 0.27 | 0.03 |

All units are in grams/liter; 1st and 2nd solutions contain 660 g/l $H_3PO_4$ and 818 g/l $H_2SO_4$; 3rd and 4th solutions contain 700 g/l $H_3PO_4$ and 863 g/l $H_2SO_4$.

**Table 17. $CrO_3$ in Chromium Plating Solutions - Experimental Analysis Data**

| $CrO_3$ Values (Actual) | Exp. t | | Exp. Mean (n=6) | | Exp. s.d. (n=6) | |
|---|---|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor | Asoma | Tracor |
| 245/245 | 2.0 | 0.5 | 245.3 | 245.7 | 0.5 | 2.7 |
| 255/255 | 0.0 | 1.2 | 255.7 | 256.7 | 0.5 | 2.4 |

All units are in grams/liter except t; 1st and 2nd solutions contain 2.60 g/l $H_2SO_4$ and 1.88 g/l Fe; 3rd and 4th solutions contain 2.80 g/l $H_2SO_4$ and 5.63 g/l Fe.

**Table 18. $H_2SO_4$ in Chromium Plating Solutions - Experimental Analysis Data**

| $H_2SO_4$ Values | Exp. t | | Exp. Mean (n=6) | | Exp. s.d. (n=6) | |
|---|---|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor | Asoma | Tracor |
| 2.60/2.60 | 0.2 | 0.7 | 2.58 | 2.65 | 0.08 | 0.11 |
| 2.80/2.80 | 0.0 | 0.3 | 2.79 | 2.74 | 0.08 | 0.16 |

All units are in grams/liter except t; 1st and 2nd solutions contain 245 g/l $CrO_3$ and 1.88 g/l Fe; 3rd and 4th solutions contain 255 g/l $CrO_3$ and 5.63 g/l Fe.

**Table 19. Fe in Chromium Plating Solutions - Experimental Analysis Data**

| Fe Values (Actual) | Exp. t | | Exp. Mean (n=6) | | Exp. s.d. (n=6) | |
|---|---|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor | Asoma | Tracor |
| 1.88/1.88 | 0.3 | 1.2 | 1.92 | 1.81 | 0.22 | 0.06 |
| 5.63/5.63 | 0.1 | 1.2 | 5.57 | 5.59 | 0.26 | 0.09 |

All units are in grams/liter except t; 1st and 2nd solutions contain 245 g/l $CrO_3$ and 2.60 g/l $H_2SO_4$; 3rd and 4th solutions contain 255 g/l $CrO_3$ and 2.80 g/l $H_2SO_4$.

**Table 20. $H_3PO_4$ in Polishing Solutions - Experimental Analysis Data**

| $H_3PO_4$ Values (Actual) | Exp. t | | Exp. Mean (n=6) | | Exp. s.d. (n=6) | |
|---|---|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor | Asoma | Tracor |
| 660/660 | 4.1* | 0.5 | 659.7 | 659.7 | 1.2 | 6.9 |
| 700/700 | 0.3 | 0.9 | 700.2 | 700.5 | 1.2 | 4.5 |

*Did not pass t-test but range of mean is only 2.0 g/l.
All units are in grams/liter except t; 1st and 2nd solutions contain 818 g/l $H_2SO_4$ and 3.75 g/l Fe; 3rd and 4th solutions contain 863 g/l $H_2SO_4$ and 11.25 g/l Fe.

**Table 21. $H_2SO_4$ in Polishing Solutions - Experimental Analysis Data**

| $H_2SO_4$ Values (Actual) | Exp. t | | Exp. Mean (n=6) | | Exp. s.d. (n=6) | |
|---|---|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor | Asoma | Tracor |
| 818/818 | 0.0 | 2.2 | 817.7 | 817.3 | 0.8 | 7.5 |
| 863/863 | 0.4 | 0.2 | 862.5 | 857.5 | 1.0 | 6.6 |

All units are in grams/liter except t; 1st and 2nd solutions contain 660 g/l $H_3PO_4$ and 3.75 g/l Fe; 3rd and 4th solutions contain 700 g/l $H_3PO_4$ and 11.25 g/l Fe.

**Table 22. Fe in Polishing Solutions - Experimental Analysis Data**

| Fe Values (Actual) | Exp. t | | Exp. Mean (n=6) | | Exp. s.d. (n=6) | |
|---|---|---|---|---|---|---|
| | Asoma | Tracor | Asoma | Tracor | Asoma | Tracor |
| 3.75/3.75 | 1.0 | 1.5 | 3.75 | 3.79 | 0.26 | 0.06 |
| 11.25/11.25 | 0.3 | 0.8 | 11.18 | 11.20 | 0.24 | 0.03 |

All units are in grams/liter except t; 1st and 2nd solutions contain 660 g/l $H_3PO_4$ and 818 g/l $H_2SO_4$; 3rd and 4th solutions contain 700 g/l $H_3PO_4$ and 863 g/l $H_2SO_4$.

**Table 23. Experimental Wastewater Detection Limits For Standard Chromium Plating Solutions**

| | Asoma | Tracor |
|---|---|---|
| Cr as $CrO_3$ | 75 | 100 |
| S as $H_2SO_4$ | 100 | 500 |
| Fe as Fe | 100 | 50 |

All units are ppm.

**Table 24. Experimental Wastewater Detection Limits For Standard Polishing Solutions**

| | Asoma | Tracor |
|---|---|---|
| P as $H_3PO_4$ | 750 | 1000 |
| S as $H_2SO_4$ | 750 | 1000 |
| Fe as Fe | 500 | 100 |

All units are ppm.

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