

ELIMINATION OF CHROMIUM OXIDATION FOR EFFECTIVE CHROMIC OXIDE DETECTIONS

by

M. HOOKS,* MICHELLE HAYES AND RALPH MAENDLE

Eagle Ottawa by Lear, Research and Product Development

2930 AUBURN ROAD, ROCHESTER HILLS, MI

ABSTRACT

Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) was used to accurately determine the Chromic Oxide content in 90 total Wet Blue, Crust, and Finished Leather samples. Accuracy was verified on each sample by testing retained composite material using ASTM D2807 Perchloric Digestion / Sodium Thiosulfate Titration Method. The ICP-OES Method correlated to ASTM D2807 with less than 2% deviation from the averaged mean value and less than 3% deviation from the averaged standard deviation value. The Chromic Oxide mean values for ASTM D2807 and ICP-OES were $3.11 \pm 0.70\%$ and $3.17 \pm 0.68\%$ respectively. The new method maintains a highly consistent statistical capability with Cpk at 2.15 vs. 2.17. Oxidation of chromium in leather samples is not required for chromic oxide detection. Perchloric acid more than doubles the required consumables cost, test time and hazard required to validate chromic oxide levels in leather materials. The ICP-OES method eliminates the crystal formation explosion hazard and chlorinated waste environmental hazards associated with Perchloric acid. Replacing ASTM D2807 with the proposed method by tannery validation laboratories is cheaper, faster, safer and more environmentally sustainable than titration by our classic technique.

INTRODUCTION

The Eagle Ottawa (EO) team purchased an ICP-OES in order to improve capability, create safe-working conditions, and create cost savings. The idea stemmed from a problem with our auto-titration equipment after ten years of service. We considered regular replacement as well as additional options, like manual titration, Atomic Absorption (AA) and the ICP-OES. The time savings and elimination of operator error were proven useful; therefore continuation of automated detection was justified. Warranty issues and product changes occurring across the globe encouraged us to increase our capability with

the purchase of either AA or ICP-OES. The Eagle Ottawa Product Development (EOPD) team evaluated these pieces of equipment with suppliers. The case was made that through the elimination of external Substance of Concern (SOC) testing and perchloric acid use, the ICP-OES would be a justified purchase saving up to Twenty-thousand dollars per year and maximizing our capability as it applies to compositional testing. The ICP-OES was selected as the replacement equipment for our chromic oxide in leather testing because of additional compositional testing capabilities.

Chromic Oxide detection is important to the leather business due to trivalent chromium salts used in the tanning process. We use the classical titration method D 2807 principles because it is an accurate test method that has been supported by the ALCA since 1959 (ASTM D2807 page 2). In order to satisfy confidence in our testing capability to ASTM D 2807 before testing with ICP-OES, we sent samples to external labs for Round Robin testing. Verification of our ASTM D2807 method capability evidenced our ability to complement ASTM 2807 by ICP-OES.

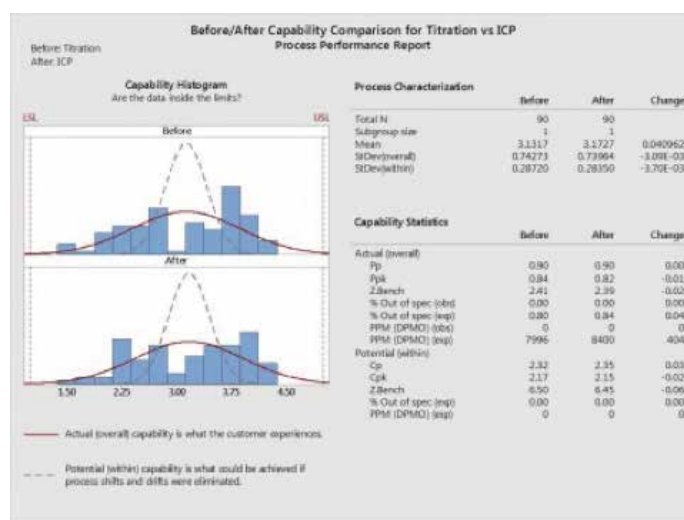


Figure 1. Statistical Summary of Test Method Capability Results.

*Corresponding author email address: Hooksm@eagleottawa.com

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The EOPD Wet End Lab Team set a goal to develop a method for determining chromic oxide content in leather using ICP-OES while eliminating the required use of Perchloric acid and improving test turnaround time. Eliminating the perchloric acid improves test safety conditions, delivers a cost-savings of four-point-four thousand dollars per thousand tests run, and eliminates the cost of a ten thousand dollar explosion resistant perchloric acid hood. In addition, the elimination of Perchloric acid eliminates hexavalent chrome generated by chromium oxidation and chlorinated waste / gas associated with the normal chromic oxide digestion. The improved test time due to a milder digestion and less testing steps, improves overall lab output. These potential cost savings which average 6 dollars per test and enhanced test capabilities made a valid business case that would generate immediate return from the acquisition of an ICP-OES.

EXPERIMENTAL METHOD

Four studies were designed for evaluating the Chromic Oxide in Leather by digestion methods and result capability.

Study 1

The first study (Figure 2) evaluated the new ICP Digestion test methods' correlation with ISO 5398 and ASTM D 2807. This was to determine if Perchloric acid was a test requirement. Four samples were tested ten times using the five methods below:

1. ISO 5398 (Ash sample then detect by Colorimetry)
2. ISO 5398 / ICP (Ash sample then detect by ICP-OES)
3. New ICP (Non-Perchloric Digestion then detect by ICP- OES)
4. ASTM D2807 / ICP (Perchloric Digestion then detect by ICP-OES)
5. ASTM D2807 (Perchloric Digestion)

Study 2

The second study served as a benchmark for assessing the repeatability and reproducibility of the test methods of highest interest. This study assessed the ASTM D 2807 method and the new ICP Digestion method with three operators and 10 samples run three times each.

Study 3

The third study served as a measure of the test methods capability over time. The ASTM D 2807 and new ICP digestion method were run on 130 samples each by one operator.

The Method steps for the classical titration referenced the ASTM D 2807 test method.

The method steps for the ICP Digestion method used the method steps listed below.

ICP-OES Detection Method

A) ICP Parameters/ Settings

- Plasma View: Radial
- Calibration: External
- Flush Time: 60 seconds
- Flush Pump Speed 45 rpm
- Analysis Pump Speed: 45 rpm
- Pump Stabilization Time: 0 seconds
- RF Power: 1350 Watts
- Aux Gas Flow: 1.5 L/min
- Nebulizer Gas Flow: 0.75 L/min
- Low WL Range
- High WL Range

B) ICP Digestion Method

- 1) Pre-dry ground composite leather sample 4 to 24 hours at 100 Celsius, then desiccate 1 hour.
- 2) Preheat hot plate to 180 °C.
- 3) Weigh 0.30 +/- 0.05 grams of leather on analytical scale into 500 mL Erlenmeyer flask. Add 3 glass boiling beads.
- 4) Add 10 mL of nitric acid
- 5) Add 10 mL of sulfuric acid
- 6) Heat samples on hot plate for ten minutes.
- 7) Remove sample from hot plate and let sit in hood for 3 minutes.
- 8) Dilute sample with deionized water until 500 mL line is reached.
- 9) Select desired preset ICP chromium test method and warm plasma to its designated parameters for 20 minutes before use.
- 10) Program ICP-OES Autosampler sequence method for samples and insert ICP tubed samples in their proper slot.
- 11) Prepare standards for calibration at 7 levels, then insert in proper ICP tube slot.
 - a) 0.2 ppm – Dilute with water
 - b) 0.5 ppm – Dilute with water
 - c) 1.0 ppm – Dilute with water
 - d) 3.0 ppm – Dilute with water
 - e) 10.0 ppm – Dilute with water

- f) 12.0 ppm – Dilute with water
- g) 16.0 ppm – Dilute with water
- 12) Prepare quality control 8 ppm standard. Dilute with D.I.
- 13) Run programmed sequence on samples.
- 14) Calculate final chromic oxide content in each sample using the ICP Chromium Content.
- 15) Report results.

RESULTS

The experimental results showed that the chromic oxide detection method by ICP-OES is an acceptable compliment to the previously accepted chromic oxide detection methods, ISO 5398 and ASTM D 2807. Study one assessed 5 methods and the final mean and standard deviation values were within the +/- 0.2 percent deviation allowed for all methods. The purpose of study two was to assess the ability of the new ICP-OES digestion method to complement the normal titration method, ASTM D2807. We gauged the methods in study two by introducing multiple operators and a larger sample size (N) as variables, the deviation in average results and average standard deviation were still within the accepted +/- 0.2 percent deviation allowed. Study two was also used for statistical assessment of capability between the methods. The capability assessment value (Cpk), results were 2.15 for ICP-OES detection and 2.17 for ASTM D 2807. This means that both methods are statistically capable because they have Cpk above 1.67, and have the same overall incumbent error because a Cpk difference of 0.02 is negligible. Study three showed us that testing over an extended time period, a large amount of samples and changes in batches of chemicals used for testing, the final results are still within the +/- 0.2 percent deviation limit. The new ICP-OES method is a good complement to previous chromic oxide in wet blue, crust, and leather material test methods.

Study four observed the bottom detection limits of both methods. The purpose was to see if we could consistently measure non-chrome leather using ICP-OES and determine if the numbers aligned with ASTM D 2807. We found that the values for both methods were within +/- 0.04 percent deviation and at the limit of detection; these differences in error were considered negligible. The titration method gave consistent results between different non-chrome leathers. The ICP-OES method was more accurate from sample to sample. There was a wider spread in results from sample to sample when testing with ICP-OES as seen in Figure 6. The ICP-OES can discriminate results between non-chrome leather samples more than the titration method, but both sets of results have less than 0.04% deviation, so each method is statistically capable of testing chromic oxide content in non-chromium leathers.

Study 1

- 5 Methods, 1 Operator, 4 Samples, 10 times each

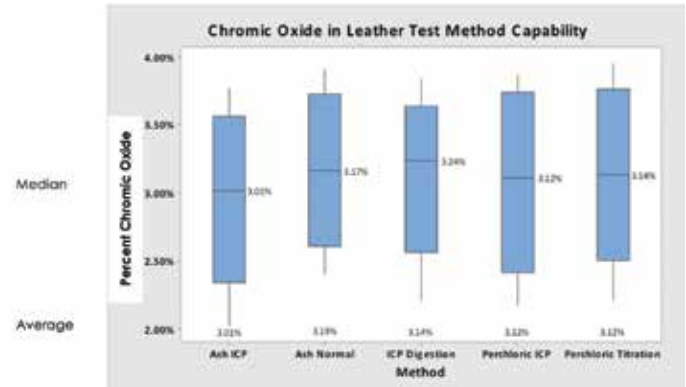


Figure 2. Boxplot of First Study.

Study 1 results showed that all methods correlate well, with less than 0.2 percent average difference in average chromic oxide percent.

Study 2

- 2 Methods, 3 Operator, 10 Samples, 3 times each

Capability Comparison for Titration vs ICP Process Performance Report		
	Titration	ICP
Total N	90	90
Mean	3.1317	3.1727
StDev(overall)	0.74273	0.73964
Cpk	2.17	2.15

Figure 3. Statistical Summary of Second Study.

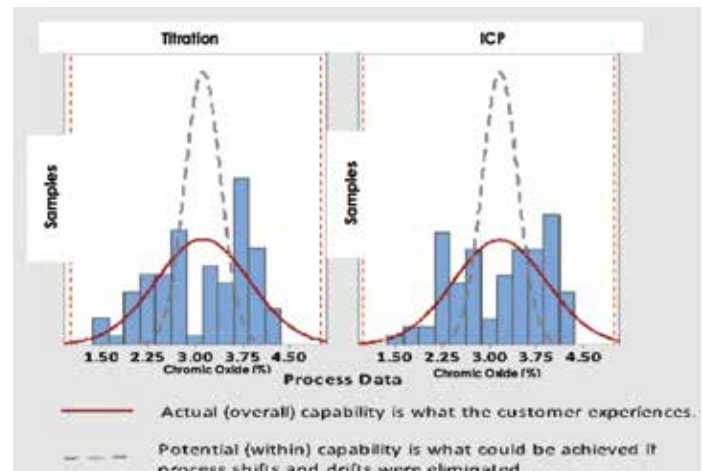


Figure 4. Histogram of Second Study.

Study 2 results showed that both methods correlate well, with less than 0.2 percent average difference in average chromic oxide percent. The most critical requirement was that the Cpk values were almost identical between methods.

Study 3

- 2 Methods, 1 Operator, 130 Samples each
- 7-month time study on ICP Chromic Oxide Test Method (260 tests run total)
- Random sample types (Wet Blue, Crust, and Finished Leather)

Study 3 results showed that both methods correlate well, with less than 0.2 percent average difference in average chromic oxide percent.

Study 4

- 2 Methods, 1 Operator, 10 Samples, 3 times each

Study 4 results showed that both methods correlate well within the range of detection at the bottom of the detection limit. Although, multiple LOTs of non-chrome leather material samples will give you the same results by titration, multiple

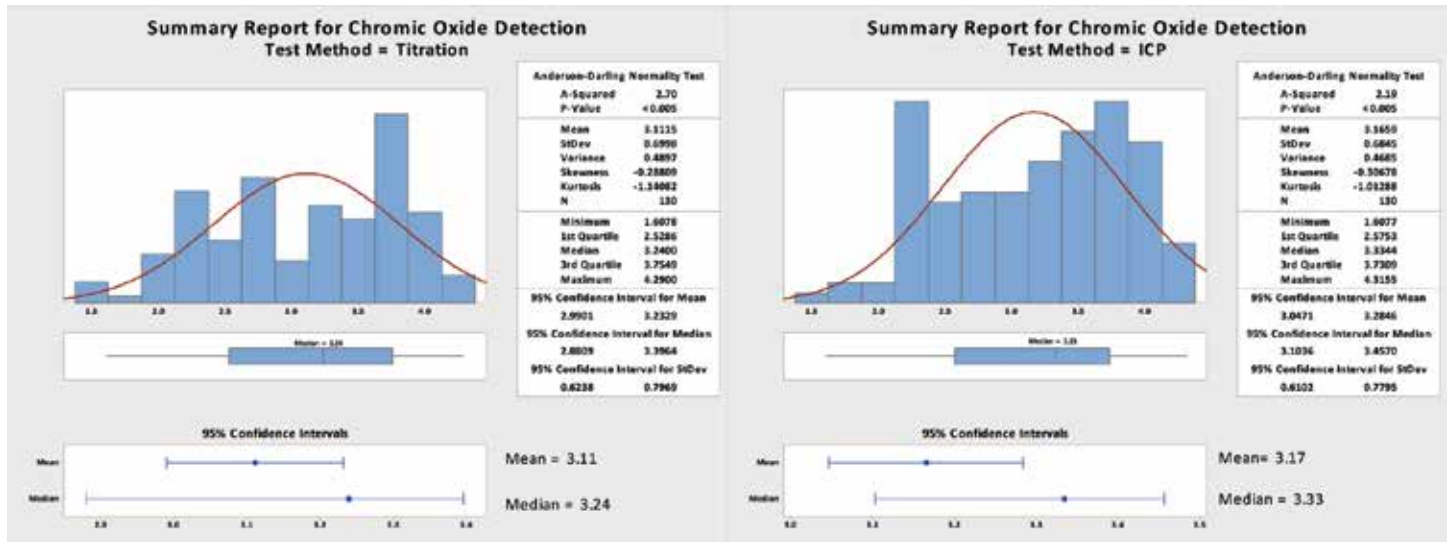


Figure 5. Statistical Summary of Third Study.

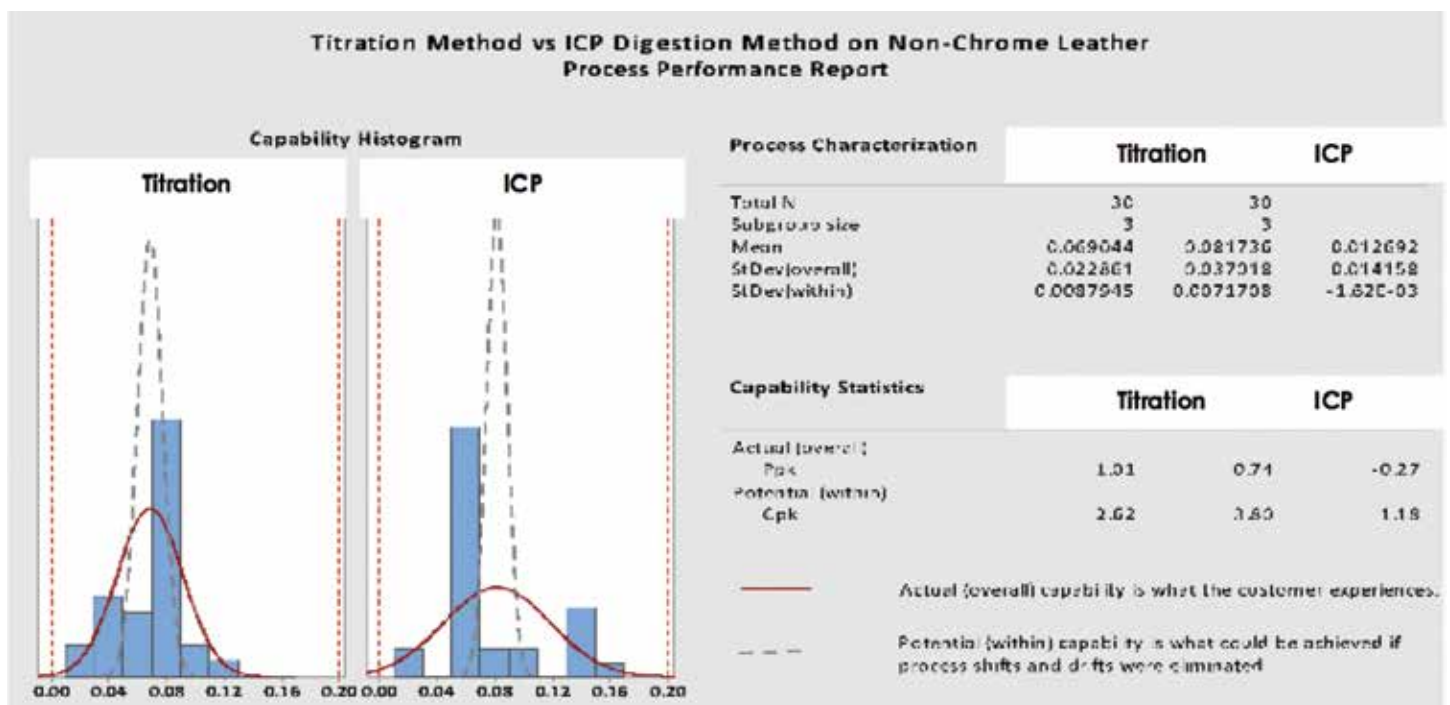


Figure 6. Statistical Summary of Fourth Study.

LOTs of non-chrome leather samples will have a larger spread of results when detecting by ICP-OES method. Results show that the ICP-OES has greater discrimination between chromic oxide levels between batches of materials with below 0.2% chromic oxide content.

DISCUSSION

The classical chromic oxide in Leather titration test method ASTM D 2807 (D 2807) uses perchloric acid and takes approximately 4 hours for complete testing of 12 samples. The EO Product Development team developed a test method using ICP OES for measuring chromic oxide in leather that correlates well to ASTM D 2807 without use of perchloric acid and requires two hours test time for 12 samples. We improved leather chemist working conditions and reduced negative impacts on the global environment by eliminating the use of oxidizers and elemental chlorine in detection of chromic oxide in leather test methods. We developed a method that can be used for Chromic Oxide detection in non-chrome and chromium leathers after purchasing the ICP-OES. We cut the required cost of chemical leather labs by elimination of water washed fume exhaust hoods for perchloric acid use, labor costs based on test-time reduction and consumable costs based on the elimination of perchloric acid. The lab team created a

test method that only uses 10 mL each of nitric acid and sulfuric acid for a 10 min digestion, reducing chemicals and detection time in order to allow for larger sample throughput. After running 270 samples for method comparison, we found the average result for the new ICP method was 3.17 +/- 0.68, and for the titration method the average was 3.11 +/- 0.70. The new method maintains a highly consistent statistical capability with Cpk at 2.15. This proved that there is no substantial difference between the methods and that the newer, safer method is a sufficient complement/replacement for ASTM D2807. The industry should consider this when considering the improvements to their compositional testing operations or starting a new chromic oxide in leather detection lab because we have proven this is a better way.

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