THE EFFECT OF ORGANIC ACIDS AND AMINES IN CHROMIUM (VI) DETERMINATION

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Introduction

There has been much debate over results obtained from the analysis for hexavalent chromium (Cr VI) in soils and leathers\(^{(1)}\). A paper titled “Organic Acids and Amines Produce Colour with Diphenylcarbazide Determinations” by Kallenberger and Hernandez was presented at the IULTCS Congress in Cancun in 2003\(^{(2)}\). The paper suggested that organic acids and amines may give false positives in Cr (VI) determinations. There was considerable interest in the presentation and it was concluded that further investigation was required\(^{(3)}\). The work presented here further examines the effect of simple organic acids and amines on Cr (VI) determinations obtained using the IUC 18 method\(^{(4)}\).

The diphenylcarbazide Cr (VI) method used by Bartlett and James in 1979\(^{(5)}\) was also tested for potential false positive results from spikes of organic acid and amines.

Experimental

The IUC 18 chromium (VI) determination method consists of an extraction phase where the soluble chromium VI is leached from the sample at pH 7.5 to 8. The Cr (VI) in solution oxidises 1,5-diphenylcarbazide to 1,5-diphenylcarbazone to give a red/violet complex with chromium. The colour development is highly dependent on pH and so conditions must be monitored carefully throughout the analysis.

Various organic acids and amines were added to the IUC 18 extraction solution (5.1)\(^{(4)}\) and any colour development was monitored throughout the Cr VI determination procedure. No actual leaching of leather was performed. The test compounds were spiked into the extraction solution and the analysis was completed.

The compounds tested to determine their potential to generate false positive were:

**Organic acids**
- Acetic acid
- Propionic acid
- Butyric acid

**Amines**
- Methylamine
- Ethylamine
Summary of Tests:

In this work, the Blank (7.4 IUC 18) refers to a 25 ml volume containing 0.5 ml of diphenylcarbazide solution (5.2), and 0.5 ml of phosphoric acid (5.3) and extraction solution (5.1) to make 25ml volume.

IUC 18 Method:
1. Blank
2. Blank with 0.2ml glacial acetic acid substituted for phosphoric acid
3. Blank with 0.5g potassium propionate substituted for phosphoric acid
4. Blank with 0.4ml 2,2 dimethyl butyric acid (98%) acid substituted for phosphoric acid
5. Blank with 0.5ml butyric acid substituted for phosphoric acid
6. Blank with 5g rancid butter (butyric acid)
7. 0.5ml diphenylcarbazide solution + 0.5ml butyric acid (99%)
8. 0.5ml diphenylcarbazide solution + 0.5g potassium propionate
9. 0.5ml diphenylcarbazide solution + 0.5ml glacial acetic acid
10. 0.5ml diphenylcarbazide solution + 0.5ml methanolamine (36% solution in water)
11. 0.5ml diphenylcarbazide solution + 0.1g ethylamine hydrochloride (98%).
12. Blank
13. Blank containing 20ppm Cr VI
14. Blank containing 20ppm Cr VI with 0.2ml butyric acid
15. Blank containing 20ppm Cr VI with 0.2g potassium propionate
16. Blank containing 20ppm Cr VI with 0.2ml methylamine (36% solution in water)
17. Blank containing 20ppm Cr VI with 0.2g ethylamine hydrochloride (98%)
18. Blank containing 20ppm Cr VI with 0.2ml glacial acetic acid

Bartlett and James Chromium Oxidation test method
19. Diphenylcarbazide Cr VI test + 0.2ml glacial acetic acid
20. Diphenylcarbazide Cr VI test + 0.2g potassium propionate
21. Diphenylcarbazide Cr VI test + 0.2ml butyric acid (99%)
22. Diphenylcarbazide Cr VI test + 0.2ml methanolamine (36% solution in water)
23. Diphenylcarbazide Cr VI test + 0.2g ethylamine hydrochloride (98%)

Results

Test 3 showed that potassium propionate forms a pink colour with 1,5-diphenylcarbazide, at pH 8, but when the pH is lowered to 4.4 with the IUC 18 standard amount of phosphoric acid, the colour dissipates.

Tests 7-11 showed that in the presence of the diphenylcarbazide solution alone, all of the organic acids and amines tested give a pink colour reaction with the 1,5-diphenylcarbazide. However with the addition of the extraction solution and phosphoric acid, as per the IUC18 method, the colour dissipates.

The tests were repeated with a 1ml spike of 1,000ppm Chromium VI standard solution (K₂Cr₂O₇) in the extraction solutions added prior to the addition of the diphenylcarbazide and phosphoric acid solutions. The spike gave a final concentration of 20ppm in the test solution. The absorbance at 540nm was no greater than the control in any of the samples with organic acid or amine spikes; hence no oxidation of the 1,5-diphenylcarbazide occurred as a result of the organic acids or amines. In all cases the pH of the solutions was adjusted with phosphoric acid to match the pH of the Blank solution containing 20ppm of Cr VI (Test 13).

Tests 19-23 used the Bartlett and James chromium oxidation test; no false positives were observed with any of the tested reagents.
Table 1: The effect of different reagents on the colour development in various Cr VI test methods.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Test Method</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Soil Test*</td>
<td>IUC 18</td>
<td>Diphenylcarbazide solution**</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>n</td>
<td>n</td>
<td>y</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>n</td>
<td>n</td>
<td>y</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>n</td>
<td>n</td>
<td>y</td>
</tr>
<tr>
<td>Methylamine</td>
<td>n</td>
<td>n</td>
<td>y</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>n</td>
<td>n</td>
<td>y</td>
</tr>
</tbody>
</table>

n: indicates no colour development was observed with the tested reagent
y: indicates a colour development was observed with tested reagent
* Bartlett and James chromium oxidation test method\(^5\)
** 1.0 g 1,5-diphenylcarbazide is dissolved in 100 ml acetone and made acidic with one drop of glacial acetic acid

Conclusion and Discussion

None of the organic acids or amines tested generated false positives using the IUC 18 standard method.

Tests did show that the diphenylcarbazide solution (5.2) reacted with the organic acids and amines resulting in colour development. However, the colour was pH dependent and when the extraction solution (5.1) or phosphoric acid solution (5.3) was added, the pink/red colour dissipated in all cases.

The Kallenberger and Hernandez paper is correct in stating that simple organic acids and amines react with diphenylcarbazide to produce a pink colour. However it has been found that if the IUC 18 standard method is adhered to, organic acids and amines will not produce false positives in Cr VI determinations.

These findings do not alter the fact that concerns about Cr VI content in leather are unjustified as discussed by Cory\(^6\). As recently stated by Long\(^7\), the criteria for setting limits in materials should be based on the risk to the manufacturer and consumer, and CEN BT 132 is currently considering the effect of Cr VI on the human body. Reports of Health-Based Soil Action Levels\(^8\) and case studies involving human exposure to Cr VI in soil and ground water\(^9\) put the relative toxicity of Cr III and VI into perspective. Cr VI is more toxic than Cr III but low levels can be tolerated and are not carcinogenic. The human studies showed that the gastrointestinal tract can reduce ingested Cr VI to Cr III at concentrations up to 10 ppm Cr VI and soil concentrations of 1240 ppm Cr VI do not elicit allergic contact dermatitis in over 99.9% of the general population. It is acknowledged that about 0.5% of the population is sensitive to chromium but chrome tanned leather has been worn for over 100 years and this sensitivity has been managed.
References


