# Determination of Chromium in Collected Leather Samples and Tannaries Waste by Spectroscopic Techniques.

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**Summary:** Chromium was extracted from collected leather samples by two different methods and in the extracted solution chromium was determined by U.V./Vis and atomic absorption methods. The chromium values in the extracted solution of both methods and using a rival SLC method were compared.

Speciation studies were also carried out in this paper and were applied to the collected water samples. For spectrophotometric determination of Cr(III), benzohydroxamic acid (BHA) was chosen as chelating agent, while for Cr(VI), diphenylcarbazide was chosen. Limits of detection of the two methods was also investigated and was found to be 50 ppb for Cr(III) and 15 ppb for Cr(VI). The interferences effect of Cr(VI), $CU^{2+}$, $Zn^{2+}$, Mo(VI) and V(V) were also investigated on Cr(III) determination using BHA as a chelating agent.

## Introduction

The heavy metals like chromium, copper, molybdenum etc are found in ore deposits and are also found in various compartments of the universe at trace level. Detailed knowledge and reliable data on their occurance, oxidation state and behaviour in the various stages of their participation in biogeochemical cycles are not always available. These biochemically essential elements at various threshold values are closely associated with various enzymatic systems, which play an essential role in different stages of metabolism. They begin to become progressively toxic [1] when threshold values are exceeded and can in some cases display carcinogenic effects [2].

Chromium, which is regarded as a particularly toxic metal, is extensively used industrially, for example in electroplating for the manufacture of alloys (especially stainless steel) and in the manufacture of corrosion inhibitors. Chromium compounds are widely used as a mordant in textile dyeing, in the tanning of leather and in paint pigments. Industrial effluents can, therefore contain significant quantities of chromium. The presence of chromium even in trace quantities in sea or river water can have a toxic influence on aquatic life.

Chromium exists mainly in two oxidation states in solution, Cr(III) and Cr(VI). Cr(III) which is less toxic than Cr(VI) and can exist in a variety of complexed or hydrolysed forms, may be associated with particulate matter. The environmental consequences of long term exposure to such oxidation states are uncertain, but chromium seems to interfere with the enzymatic sulphur uptake of cells [3] affecting

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the lungs, liver and kidneys [4-5].

To protect fresh water aquatic life the concentration of Cr(III) and Cr(VI) should not exceed 44 µg dm$^{-3}$ and 21 µg dm$^{-3}$ respectively as recommended by U.S. environmental protection agency (E.P.A.) [6]. The maximum concentration of Cr(VI) presently permitted in drinking water is 50µg dm$^{-3}$ as recommended by EPA.

In Pakistan, the major source of chromium pollution of the aquatic environment is the waste disposal from the tannaries. The work presented in this paper is an attempt to estimate the amount of Cr present in leather and its waste, with the view to estimate the amount of pollution caused by the tanning industry.

**Experimental**

*Apparatus:*

A Pye unicam atomic absorption spectrophotometer model SP-191 and Jasco, digital double beam U.V./Vis spectrophotometer were used for determination of chromium. WPA model 660, pH meter was used for pH measurements.

*Reagents:*

All the reagents used, except BHA, were of analaytical grade purity and were purchased commercially, while BHA was synthesized in our own laboratory by the literature method [7]. Doubly distilled water was used throughout the analysis.

*Solutions:*

(1) 100 ppm stock solution of Cr(VI) was prepared by dissolving an appropriate amount of $K_2 Cr_2 O_7$ in distilled water and diluting to the mark.

(2) Diphenyl Carbazide Solution:

0.1 % diphenyl carbazide (DPC) solution was prepared by dissolving 0.1 g of DPC in minimum methanol and making up the volume to 100 ml with distilled water.

(3) Benzohydroxamic acid Solution:

0.1 % BHA solutions were prepared by dissolving 0.1 g of BHA in 100 ml distilled water.

Procedure:

1. Preparation of Solution of Spectrophotometric determination of chromium in leather sample [8]:

About 100-300 mg dried leather is taken in the quartz crucible. The sample is carefully carbonized over a low flame. The residue is moistened with a few drops of sulphuric acid and heated on hot plate until all fumes have disappeared. The addition of sulphuric acid and fumming off processes repeated once again. The crucible is then heated in muffle furnace at 800°C for 30 minutes. After cooling, 2 ml of perchloric acid is added, the crucible is covered with a watch glass and heated for 1 hour on a hot plate at 250°C. After cooling the sample is dissolved in water. All chromium of the sample is now in Cr(VI) form. The pH of the solution is adjusted to 1.3. Colour is developed by the addition of 1 ml of 0.1 % DPC. The solution is then diluted to 100 ml in volumetric flask and the absorbance is measured at 540 nm against a blank solution prepared by the same method. A calibration plot is prepared for the standards in the concentration range of 15-70 ppb., using the same procedure as for the samples.

2.  Preparation of sample for atomic absorption determination of chromium:

A weighed amount of ground leather is taken into conical flask, to which 5 ml conc. hydrochloric acid and some carborundum beads are added. The flask is heated with a heating plate under reflux with a water cooled condenser. The flask is heated until the colour of the solution is clear light green to colourless. The flask is then cooled to room temperature and the condenser is flushed with small amount of distilled water. The solution is diluted to 100 ml with distilled water. In this case chromium in solution was in Cr(III) form. The solution is then directly aspirated into the atomic absorption flame after dilution and the reading were taken at optimum wavelength and flame temperature. Cr(III) standard were prepared from chromic nitrate in the

concentration range of 1-10 ppm. The working standards were treated in the same way as the samples.

**Results and Discussion**

The effect of pH on chelation of Cr(III) with BHA was studied for the spectrophotometric determination of Cr(III) using BHA. pH 9 was found to be the optimum pH. The interferences effect of Cr(VI) was studied on determination of Cr(III) by this method. It was found out that Cr(VI) at any concentration does not interfere at all.

The interferences effect of Cu(II), Mo(VI), V(V) and Zn(II) were also studied on the determination of Cr(III) by this method. The results are shown in tabulated form in tables 1-4. All these metals do interfere even at trace levels. Therefore if Cr(III) is to be determined by this method

Table-1: Showing the Interference effect of Cu conc., on Cr(III) determination by spectrophotometric method using BHA as chelating agent.

| Solution | Interferent Added | Absorbance | % Recovery |
|---|---|---|---|
| 5 ppm of Cr(III) | None | 0.65 | 100.00 |
| " | 10 ppb of Cu | 0.74 | 118.96 |
| " | 50 " | 0.75 | 119.74 |
| " | 100 " | 0.75 | 120.14 |
| " | 500 " | 0.75 | 120.14 |
| " | 1000 " | 0.81 | 128.57 |

Table-2: Showing the interferences effect of Mo on Cr(III) determination by spectrophotometric method using BHA as chelating agent.

| Solution | Interferent Added | Absorbance | % Recovery |
|---|---|---|---|
| 5 ppm of Cr((III) | None | 0.65 | 100.00 |
| " | 10 ppb of Mo | 0.71 | 109.23 |
| " | 50 " | 0.77 | 118.46 |
| " | 75 " | 0.91 | 114.00 |
| " | 100 " | 0.95 | 146.15 |
| " | 500 " | 0.74 | 113.84 |
| " | 1000 " | 0.99 | 152.30 |

Table-3: Showing the interferences effect of V on Cr(III) determination by spectrophotometric method using BHA as chelating agent.

| Solution | Interference Added | Absorbance | % Recovery |
|---|---|---|---|
| 5 ppm of Cr(III) | None | 0.66 | 100.00 |
| " | 10 ppb of V | 0.65 | 98.48 |
| " | 50 " | 0.73 | 110.60 |
| " | 75 " | 0.79 | 119.69 |
| " | 100 " | 0.88 | 133.33 |
| " | 500 " | 0.74 | 122.12 |
| " | 1000 " | 1.25 | 189.39 |

Table-4: Showing the interferences effect of Zn on Cr(III) determination by spectrophotometric method using BHA as chelating agent.

| Solution | Interference Added | Absorbance | % Recovery |
|---|---|---|---|
| 5 ppm of Cr(III) | None | 0.64 | 100.00 |
| " | 10 ppb of Zn | 0.62 | 96.00 |
| " | 50 " | 0.65 | 101.56 |
| " | 100 " | 0.56 | 87.50 |
| " | 500 " | 0.76 | 118.75 |
| " | 1000 " | 1.27 | 198.43 |

in the presence of these metals, prior separation of these metals would be essential. Limits of detection of Cr(III) by this method were investigated and was found to be 50 ppb.

Similarly conditions were optimised for the spectrophotometric determination of Cr(VI) using DPC as chelating agent. A wavelength of 540 nm, 0.05N concentration of the solution in HCl (pH 1.3) and 1 ml of 0.1 % DPC solutions were found to be the optimum amount for Cr(VI) complexation with DPC and subsequent spectrophotometric investigation.

The effect of Cr(III) interferences on this method were investigated. No effect of Cr(III) was observed in the complexation of Cr(VI) and subsequent spectrophotometric investigation. Limit of detection for Cr(VI) was determined by this method and was found to be 15 ppb.

The waste water collected from the outlet of the two tannaries near Peshawar were subjected to Cr(III) and Cr(VI) determination by the spectrophotometric method. It was found out that the waste water were free of chromium contents. The main reason for this could be that the chromium contents were diluted by the waste water disposal from vegetable tanning. Physical properties like pH and conductivity of the collected samples were also measured. Ca(II), and Mg(II) contents were determined by a volumetric method while Na$^+$ and K$^+$ in the collected water samples were determined by the flame photometric method. The results are shown in table 5.

Solutions of the collected leather samples were prepared by two methods, that is by the lengthy and time consuming standard SLC method [8] for spectrophotometric determi-

Table-5: Showing Physicochemical properties of collected water samples.

| Location | pH | Conductivity (Siemens) | Ca mg/ml | Mg mg/ml | Na mg/ml | K mg/ml |
|---|---|---|---|---|---|---|
| Toti Tannary, sample collected from out let of tannary | 7.4 | $20 \times 10^2$ | 0.07 | 0.06 | 720 | 29 |
| Toti Tannary, Drum washing from chrome bath | 4.8 | $14.5 \times 10^2$ | 0.06 | 0.09 | 430 | 69 |
| Akhtar Tannary waste water | 7.0 | $5.3 \times 10^2$ | 0.12 | 0.01 | 200 | 9 |
| Akhtar Tannary tape water | 7.0 | $6.3 \times 10^2$ | 0.06 | 0.08 | 900 | 20 |
| Akhtar Tannary, sample from out let of tannary | 10.7 | $70 \times 10^2$ | 0.08 | 0.03 | 3950 | 85 |

Table-6: Showing comparison of chromium values by different methods.

| Sample state | % of Cr determined by U.V./Vis | | % of Cr determined by atomic absorption method | |
|---|---|---|---|---|
| | Solution prepared by SLC method | solution prepared by our own laboratory method | solution prepared by S.L.C. method | solution prepared by our own laboratory method. |
| Shaving of leather | 0.46 | 0.48 | 1.11 | 1.15 |
| 50% tanned leather | 1.01 | 1.15 | 1.44 | 1.44 |
| 100% tanned leather (1) | 1.44 | 1.80 | 1.79 | 2.08 |
| 100% tanned leather (2) | 1.73 | 2.0 | 2.90 | 3.02 |
| 100% tanned leather (3) | 1.38 | 1.65 | 1.80 | 2.00 |

nation of Cr(VI) and by the method devised in our own laboratory for determination of chromium in leather samples by atomic absorption method. The solution prepared by our own laboratory method was also subjected to U.V./Vis. analysis for comparison. The results are shown in tabulated form in table 6. From table 6, it is clear that there is a reasonably close agreement of the results of the two solution preparation methods, when the

analyses are carried out by atomic absorption method.

Further it is clear from the results that low values of Chromium are obtained, when chromium is determined in leather by spectrophotometric method, using any of the solution preparation method. This could be due to incomplete oxidation of Cr(III) to Cr(VI) which is finally determined spectrophotometrically. The so called 50 % tanned leather although contain relatively smaller quantities of chromium but is not really 50 % as compared with 100% chrome tanned leather. It is concluded that our own laboratory solution preparation method with atomic absorption determination is the best method as it is rapid and gives comparable results with the existing methods.

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