Chapter 6

EXTRACTION SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF CHROMIUM WITH TETRAPHENYLARSONIUM CHLORIDE

Introduction:

Several reagents are known which are used for the determination of small amounts of chromium by spectrophotometric method. The most sensitive reaction for the determination of chromium is one between S-diphenyl carbazide and chromium(VI) in acid solution. The resulting red violet species is reported to be extractable by organic solvents like isoamyl alcohol, chloroform, and cyclohexanol and was used in recent years for spectrophotometric determination of chromium(VI) using prior separation methods. Other reagents used for the determination of chromium are NH₄-pyrrolidine-1-carbodithioate, uramildiacetic acid, 3-hydroxy-4-(2-hydroxy-1-naphthylazo) naphthalene-1-sulphonic acid and mercaptoacetic acid. Majumder and De, however, used 2-thenoyltrifluoroacetone (T.T.A.) for direct spectrophotometric determination of chromium by extracting the chromium(III)-T.T.A. complex into benzene.

It has been found, following the suggestion of Alimarin and Perezhogin, that chromium(VI) forms ion-association compound with tetraphenylarsonium cation extractable into chloroform or 1,2-dichloroethane, a fact which has been reported earlier by Hala et al. Baishya and Heslop determined chromium in aluminium alloys both by neutron activation and isotope dilution analysis based on the principle of substoichiometric extraction with tetraphenylarsonium chloride.
In the present work spectrophotometric determination of chromium by extraction of its ion-pair with tetraphenylarsonium chloride into 1,2-dichloroethane was investigated. The relative ease of interconversion of chromium(III) to chromium(VI) and formation of easily extractable chromium(VI)-tetraphenylarsonium ion-pair made it possible to determine chromium in presence of most of the commonly associated elements. The method was tested in the determination of chromium in standard steel samples.

Experimental:

Apparatus:

Absorption spectrum in the particular wavelength region was taken and absorbance measurements were made with a Beckman DK-2 spectrophotometer. At times, absorbance at specific wavelength was also measured in the Hilger Uvispek Photoelectric spectrophotometer.

Reagents:

Most of the chemicals used were of analytical grade.

Solvent:

Laboratory grade 1,2-dichloroethane procured from B.D.H. was redistilled for use as solvent.

Standard chromium solution:

A stock solution was prepared by dissolving 0.3734 g of
potassium chromate (analar) in 1N sulphuric acid in a 100 ml standard flask and the volume was made up with the same acid. The solutions of lower concentrations were prepared from the stock solution by dilution with 1N sulphuric acid.

Reagent solution:

A 0.01M solution of tetraphenylarsonium chloride (Fluka A.G., Buchs SG) was prepared in doubly distilled water.

Other chemicals:

Other metal compounds used for studying interferences were ferric ammonium sulphate, cadmium sulphate, copper sulphate, mercuric chloride, ammonium molybdate, sodium tungstate, potassium permanganate, potassium thiocyanate, ammonium fluoride, sodium oxalate, sodium vanadate, sodium perchlorate and potassium antimonyl tartrate.

Preliminary studies on the extraction and spectrophotometric determination of chromium:

Absorption spectra:

The absorption spectrum of a solution of tetraphenylarsonium chromate complex in 1,2-dichloroethane obtained by extracting an acidic solution of chromium(VI) containing 100 μg of chromium with tetraphenylarsonium chloride was taken in Beckman DK-2 spectrophotometer in the region 410-330 nm against the solvent (Fig. 1). The absorption maximum
Fig. 1. Absorption spectra of tetraphenyllarsonium chromate in 1,2-dichloroethane containing 20 µg of chromium per c.c.
(A) Against solvent.
(B) The spectrum of the reagent blank against solvent.
of the complex was found to be at 363 nm. The reagent blank against solvent showed no absorption in this region. Hence all the absorbance measurements were carried out at 363 nm against solvent as reference using 1 cm quartz cell.

Variation of absorbance with acid concentration:

In order to examine the effect of acidity of the aqueous layer in the extraction of chromium, 5 ml of standard solution containing 100 μg of chromium was taken in several different separating funnels. Normality of each of the solution was made different with respect to sulphuric acid by adding varying amount of standard acid. To each of these was then added 1 ml of 0.01M tetraphenylarsonium chloride reagent. The resulting complex, in each, was extracted into 5 ml of 1,2-dichloroethane and the absorbance of the extracts were measured at 363 nm. The variation of absorbance with acidity is shown in Fig. 2.

Effect of tetraphenylarsonium chloride concentration on absorbance:

To a series of 5 ml of the standard solutions, containing 100 μg of chromium, which were made 1N with respect to sulphuric acid, 1 ml of tetraphenylarsonium chloride reagent of varying concentration was added separately in each. The resulting complex in each, was then extracted into 5 ml of 1,2-dichloroethane and the absorbance of the extracts were measured at 363 nm. Dependence of absorbance on tetraphenylarsonium chloride concentration is shown in Fig. 3.
FIG. 2. Variation of absorbance with acid concentration.

FIG. 3. Variation of absorbance with TPA-CL concentration.

FIG. 4. Variation of absorbance with time.
Variation of absorbance with time:

An aliquot containing 100 µg of chromium was taken to which 1 ml of 0.01M tetraphenylarsonium chloride reagent was added. The resulting complex was then shaken for 2 minutes with 5 ml of 1,2-dichloroethane. After extraction, absorbance of the extract at 363 nm was measured at different time intervals. The variation of absorbance with time is shown in Fig. 4.

Analytical and separation procedure:

Aliquots of the standard solution containing 50 µg to 200 µg of chromium were taken in several different separating funnels. The volume in each was made up to 5 ml by adding 1N sulphuric acid. To each of these solutions was then added 1 ml of 0.01M tetraphenylarsonium chloride reagent. The resulting mixture was then shaken for 2 minutes with 5 ml of 1,2-dichloroethane. The organic layer was separated and the absorbance was measured at 363 nm against the pure solvent. A standard calibration curve obtained by plotting these absorbance values against chromium concentration is shown in Fig. 5. The ion-pair, tetraphenylarsonium chromate, conforms to Beer's law over the concentration range of 10 to 40 µg of chromium per ml of the extract.

Different aliquots of the chromium solution, for the determination of chromium in other sample solutions, were treated in a similar manner and their 1,2-dichloroethane extracts were measured at 363 nm. The amount of chromium was then calculated from the standard calibration curve. The results which are the
FIG. 5. CALIBRATION CURVE FOR CHROMIUM

AMOUNTS OF CHROMIUM IN µg

ABSORBANCE
average of five determinations, in each case, are shown in Table 1.

Studies on interferences due to other ions in the determination of chromium:

In a separate set of experiments, an aliquot of the standard solution containing 100 μg of chromium was taken in each of the several different separating funnels. To each of these an aqueous or acidic solution of the metal ions, viz., iron(III), cadmium(II), copper(II), mercury(II), antimony(III) and the anions molybdate, tungstate, permanganate, thiocyanate, thiosulphate, fluoride, oxalate, vanadate, and perchlorate, in amounts equal to and five/three times the amount of chromium was added. The volume, in each case, was made up to 5 ml. Each solution was made 1N with respect to sulphuric acid and to these were then added 1 ml of 0.01M tetraphenylarsonium chloride reagent. The resulting mixture was extracted as above with 5 ml of 1,2-dichloroethane and the absorbance of the extract was measured at 363 nm. The results showing the recovery of chromium are given in Table 2.

Removal of interferences due to -

(a) Oxalate:

An aliquot of the standard solution, containing 100 μg of chromium was taken in two different small beakers. To each of these solutions, a solution containing 100 and 500 μg of oxalate was added separately. Each of the resulting solutions were warmed and a dilute solution of equivalent amount of potassium
permanganate was added dropwise. The solution was then treated with 2 ml of 10% ceric sulphate solution and was boiled for 10 minutes. After cooling, the solutions were transferred to two different separating funnels. The solutions were made 1N with respect to sulphuric acid and was extracted with 5 ml of isobutyl methyl ketone. Chromium in the organic phase was then back extracted with water and was made 1N with respect to sulphuric acid followed by the addition of 1 ml of 0.01M tetraphenylarsonium chloride reagent. Determination of chromium was then completed as described above.

(b) Manganese(VII):

An aliquot of the standard solution containing 100 µg of chromium was taken in two different small beakers. To each of these solutions, solutions containing 100 µg and 500 µg of permanganate was added separately. Each of these solutions was warmed with 2 to 3 drops of absolute alcohol. The resulting colourless solutions were then treated with 2 ml of 10% ceric sulphate solution. Chromium as chromate was then separated, extracted, and estimated as described above.

The results showing the recovery of chromium after removal of interferences due to oxalate and manganate ion are given in Table 3.
Determination of chromium in high speed steel and alloy steel:

0.1 g of high speed steel (No. 64b) and 0.6 g of alloy steel (No. 60b), procured from the Bureau of Analysed Samples Ltd., was accurately weighed out in two different small beakers. The alloys were then dissolved in the minimum volume of concentrated nitric acid by heating on a hot plate. To each of the cooled solution was added 2 ml of 50% sulphuric acid and was heated till the evolution of white fumes. To the resulting solutions, after appropriate dilution, were added 2 ml of 10% ceric sulphate solution and were boiled for 10 minutes. The solutions were cooled, made 1N in sulphuric acid and were extracted with 10 ml of isobutylmethyle ketone for 3 minutes. The organic extracts were washed with 1N sulphuric acid and the dichromate was then back extracted by shaking the organic layer repeatedly with distilled water. Combined aqueous solutions were transferred into two separate 100 ml standard flasks and the required amount of 50% sulphuric acid were added to make them 1N in sulphuric acid in the made up solution.

Separate aliquots from each solution were taken in different separating funnels to each of which 1 ml of 0.01M tetraphenylarsonium chloride reagent was added. Volume of the resulting solution was made 5 ml with 1N sulphuric acid and was then extracted with 5 ml of 1,2-dichloroethane. Absorbance in the organic layer was measured at 363 nm and the amount of chromium was calculated from the calibration curve. The average of a number of determinations from each sample are shown in Table 4.
Results and discussion:

Chromium(VI) forms ion-pair with tetraphenylarsonium chloride and the resulting ion-association compound which is precipitated in aqueous solution 1N in sulphuric acid was found to be soluble (extractable) in chloroform and 1,2-dichloroethane. Of the two solvents, 1,2-dichloroethane proved to be a better extractant for the ion pair which absorbed in the ultraviolet region having maximum absorption at 363 nm. Beer's law is obeyed over the concentration range 10 to 40 μg of chromium per ml of the organic phase. The sensitivity of the method was found to be 0.05 μg of chromium per ml per cm². The maximum error involved in the determination of trace quantities of chromium in absence of other ions is within 2%.

Dependence of absorbance of the tetraphenylarsonium chromate complex on various factors, viz., acidity of the aqueous layer, reagent concentration, stability of colour with time and temperature was studied.

Extraction of tetraphenylarsonium chromate complex is possible from solution which is 1N with respect to sulphuric acid. An examination of the acid concentration showed that the absorbance of the extract increases with increasing acidity and remained almost constant in between 0.8N to 1.5N and then decreases slowly beyond 1.5N. The acid concentration of the aqueous layer was, therefore, maintained at 1N.

The extraction of chromium(VI) at varying concentration of tetraphenylarsonium chloride revealed that a 0.01M aqueous solution of the reagent was found to be most suited for
quantitative extraction. One ml of 0.01M tetraphenylarsonium chloride reagent was thus found to be sufficient for the determination of 50 to 200 \( \mu g \) of chromium(VI).

The absorbance of the complex in 1,2-dichloroethane was measured at elapsed intervals of 5, 10, 30, 60, 90, 120, 140, 180, 200 and 240 minutes after extraction. The absorbance value was found to be stable up to 160 minutes. The absorbance of the complex is therefore measured within 160 minutes of its extraction. The absorbance of the complex is independent of temperature in the range 20 to 35°C.

An examination of the interfering effect of number of metal ions, viz., iron(III), cadmium(II), copper(II), mercury(II), antimony(III) in varying amounts revealed that except antimony(III), none of these ions interfered. The organic extract of chromium(VI) tetraphenylarsonium chloride complex was found to be colourless in presence of antimony(III) probably due to the reduction of chromium(VI) by antimony(III). Other metal ions did not interfere as there was no possibility of formation of their halo complexes capable of forming ion-pair with tetraphenylarsonium chloride. Similar examination with anions, having possibility of ion-pair formation with tetraphenylarsonium chloride, viz., molybdate, tungstate, permanganate, thiosulphate, thiocyanate, fluoride, oxalate, vanadate, and perchlorate were made. Of these only permanganate and thiosulphate interfered even when present in amounts equal to chromium. Oxalate interfered only slightly. Thiocyanate though did not interfere greatly in equal amount, but it interfered when present in five times excess. However, the relative ease of interconversion of chromium(III) to chromium(VI)
made it possible to separate chromium from most of the commonly associated interfering elements.

Interference due to oxalate ion was removed by potassium permanganate oxidation. Chromium was then separated from any excess permanganate by extraction with isobutyl methyl ketone from 1N sulphuric acid and it was determined subsequently by back extracting to water. Interference due to permanganate ion was removed by reduction with alcohol when both permanganate and chromate are reduced. Chromium was later oxidised with ceric sulphate in acid solution and was then separated and estimated with good recovery of chromium.

The method was used for the determination of chromium in high speed steel and alloy steel and the amount of chromium found was good with an error within 3 to 4%.

Thus the method proved to be a simple, rapid and sensitive one providing a good recovery of chromium in presence of most of the common ions.
Table 1

Extractive spectrophotometric determination of chromium

<table>
<thead>
<tr>
<th>Chromium in μg</th>
<th>% Error</th>
<th>Chromium in μg</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present</td>
<td>Found</td>
<td>Present</td>
<td>Found</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>120</td>
<td>122</td>
</tr>
<tr>
<td>50</td>
<td>50.5</td>
<td>145</td>
<td>147</td>
</tr>
<tr>
<td>70</td>
<td>71.0</td>
<td>160</td>
<td>161.8</td>
</tr>
<tr>
<td>85</td>
<td>84.5</td>
<td>180</td>
<td>177.6</td>
</tr>
<tr>
<td>100</td>
<td>98.5</td>
<td>200</td>
<td>197.5</td>
</tr>
</tbody>
</table>
Table 2

Effect of diverse ions on the determination of chromium
(100 µg) of chromium was taken in each determination.

<table>
<thead>
<tr>
<th>Interfering Ion added</th>
<th>Amount in µg</th>
<th>Chromium found (µg)</th>
<th>% Error</th>
<th>Ion added</th>
<th>Amount in µg</th>
<th>Chromium found (µg)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
<td>MnO$_4^-$</td>
<td>100</td>
<td>114</td>
<td>14</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>300</td>
<td>100</td>
<td>Nil</td>
<td>MnO$_4^-$</td>
<td>500</td>
<td>-</td>
<td>Interfered</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
<td>S$_2$O$_3^-$</td>
<td>100</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>300</td>
<td>99</td>
<td>1</td>
<td>S$_2$O$_3^-$</td>
<td>300</td>
<td>-</td>
<td>Interfered</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
<td>CNS$^{-1}$</td>
<td>100</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>300</td>
<td>100</td>
<td>Nil</td>
<td>CNS$^{-1}$</td>
<td>500</td>
<td>-</td>
<td>Interfered</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
<td>F$^{-1}$</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>300</td>
<td>100</td>
<td>Nil</td>
<td>F$^{-1}$</td>
<td>300</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>100</td>
<td>78</td>
<td>22</td>
<td>C$_2$O$_4^-$</td>
<td>100</td>
<td>102</td>
<td>2</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>300</td>
<td>-</td>
<td>No colour in the extract</td>
<td>C$_2$O$_4^-$</td>
<td>500</td>
<td>118</td>
<td>18</td>
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<tr>
<td>MoO$_4^{-2}$</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
<td>V$_3$O$_4^{-1}$</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
</tr>
<tr>
<td>MoO$_4^{-2}$</td>
<td>500</td>
<td>100</td>
<td>Nil</td>
<td>V$_3$O$_4^{-1}$</td>
<td>500</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>WO$_4^{-2}$</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
<td>ClO$_4^{-1}$</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
</tr>
<tr>
<td>WO$_4^{-2}$</td>
<td>500</td>
<td>99</td>
<td>1</td>
<td>ClO$_4^{-1}$</td>
<td>500</td>
<td>100</td>
<td>Nil</td>
</tr>
</tbody>
</table>
### Table 3

Recovery of chromium in presence of interfering ions
(100 µg of chromium was taken in each case)

<table>
<thead>
<tr>
<th>Interfering Ion added</th>
<th>Amount in µg</th>
<th>Chromium found in µg</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_2O_4^-2</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
</tr>
<tr>
<td>C_2O_4^-2</td>
<td>500</td>
<td>100</td>
<td>Nil</td>
</tr>
<tr>
<td>MnO_4^-1</td>
<td>100</td>
<td>100</td>
<td>Nil</td>
</tr>
<tr>
<td>MnO_4^-1</td>
<td>500</td>
<td>99.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### Table 4

Determination of chromium in high speed steel and alloy steel

<table>
<thead>
<tr>
<th>Samples</th>
<th>Chromium found per cent</th>
<th>Chromium present per cent</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>High speed steel (No. 64b)</td>
<td>4.4</td>
<td>4.55</td>
<td>3.3</td>
</tr>
<tr>
<td>Alloy steel (No. 60b)</td>
<td>0.72</td>
<td>0.75</td>
<td>4</td>
</tr>
</tbody>
</table>
REFERENCES


