Chapter – V

SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF SOME IMPORTANT TRANSITION METAL IONS
Section 1; Simultaneous spectrophotometric determination of titanium (IV) and molybdenum (VI)

Titanium (IV) reacts with 2-HNHBH in the pH range of 1.0 to 6.0 to form brown coloured water soluble complex. The colour intensity is maximum at the pH 2.0 (c.f. section 4.3). The complex shows $\lambda_{\text{max}}$ at 405 nm. Molybdenum (VI) reacts with 2-HNHBH giving orange coloured water soluble complex in the pH range of 1.0 to 5.0 (c.f. section 4.2) and has absorbance maximum at 450 nm.

Thus, it is clear that both Ti (IV) and Mo (VI) react with 2-HNHBH forming water soluble coloured complexes and have maximum absorbance at pH 2.0. It is, therefore, possible to determine Ti(IV) and Mo(VI) simultaneously, spectrophotometrically with 2- HNHBH. The following procedure is adopted for the purpose.

Absorption spectra

The absorption spectra of the following solutions are recorded for selecting the wavelengths for absorbance measurements.

Solution (a)

The absorption spectrum of 2-HNHBH in pH 2.0 is recorded by following the procedure in 3.a and presented in fig.5.1.1.a.

Solution (b)

The absorption spectrum of Mo (VI)-2-HNHBH complex ($5.0 \times 10^{-4}$ M) is recorded by following the procedure in 3.b and presented in fig.5.1.1.b.

Solution (c)

The absorption spectrum of Ti (IV) – 2-HNHBH complex ($5.0 \times 10^{-4}$ M) is recorded by following the procedure in 3.b and presented in fig.5.1.1.c.
Fig. 5.1.1 Absorption spectra of
a) 2-HNHBH Vs buffer blank
b) Mo (VI) – 2-HNHBH system Vs reagent blank
c) Ti (IV) – 2-HNHBH system Vs reagent blank

\[ [\text{Ti (IV)}] = [\text{Mo (VI)}] = 5.0 \times 10^{-4} \text{ M}; \text{pH 2.0} \]
From the spectra in fig. 5.1.1., it is clear that Ti (IV) shows absorbance maximum at 405 nm and Mo (VI) shows absorbance maximum at 450 nm. It is further noticed that Ti (IV) shows higher absorbance at 405 nm than Mo(VI) and less absorbance at 450 nm and vice versa. The absorbance of the mixture containing Ti(IV) and Mo(VI) either at 405 or 450 nm is equal to the sum of the absorbance values due to individual Ti (IV) and Mo (VI) species at these wavelengths. This suggests that it is possible to carry out a simultaneous spectrophotometric determination of Ti (IV) and Mo (VI) using 2-HNHBH by measuring the absorbance of the solution mixtures at 405 nm and 450 nm.

**Applicability of Beer’s law**

To establish whether Beer’s law is applicable to Mo (VI) and Ti (IV) species at 450 nm and 405 nm, the absorbance measurements for various amounts with any metal ion is made at both these wavelengths (following procedure in 3.g.). The results are presented in figs. 5.1.2. and 5.1.3.

From the linear plots it is observed that Beer’s law is obeyed for Mo (VI) in the range 0.479-4.479 µg/ml at 450 nm and 0.959 to 3.886 µg/ml at 405 nm. Ti (IV) obeys Beer’s law in the range of 0.239-2.390 µg/ml at 405 nm and 0.479 to 1.916 nm. The molar absorptivities for Mo (VI) are 0.65 ± 0.002 × 10^4 lit mol^-1 cm^-1 and 0.198 ± 0.002 × 10^4 lit mol^-1 cm^-1 respectively at 450 nm and 405 nm and similarly, for Ti (IV) they are 1.68 ± 0.002 × 10^4 lit mol^-1 cm^-1 and 0.328 ± 0.002 × 10^4 lit mol^-1 cm^-1 at 405 and 450 nm respectively.

The absorbance of the solution mixture containing Ti (IV) and Mo (VI) complex species is recorded at 405 nm and 450 nm at pH 2.0. From these absorbance values the amount of Ti(IV) and Mo(VI) are calculated using the following simultaneous equations.

\[
A_{405} = T_i \varepsilon_{405} C_{Ti} + M_o \varepsilon_{405} C_{Mo} \quad \ldots\ldots\ldots\ldots\ldots5.1.1
\]

\[
A_{450} = T_i \varepsilon_{450} C_{Ti} + M_o \varepsilon_{450} C_{Mo} \quad \ldots\ldots\ldots\ldots\ldots5.1.2.
\]
Fig. 5.1.2. Zero order absorbance Vs amount of Mo (VI) 
\[ \text{pH} = 2.0 \]

Fig. 5.1.3. Zero order absorbance Vs amount of Ti (IV) 
\[ \text{pH} = 2.0 \]
Converting concentrations into amounts (μg/ml) and solving the equation

5.1.1. we get,

\[
Ti \text{ (IV)} = \frac{A_{405} \varepsilon_{Ti}^{405} - A_{450} \varepsilon_{Mo}^{405}}{\varepsilon_{Ti}^{405} \varepsilon_{Mo}^{450} - \varepsilon_{Mo}^{450} \varepsilon_{Ti}^{405}} \times 47.9 \times 10^3 \quad \ldots 5.1.2.
\]

\[
Mo \text{ (VI)} = \frac{A_{405} \varepsilon_{Mo}^{405} - A_{450} \varepsilon_{Ti}^{405}}{\varepsilon_{Ti}^{405} \varepsilon_{Mo}^{450} - \varepsilon_{Mo}^{450} \varepsilon_{Ti}^{405}} \times 95.9 \times 10^3 \quad \ldots 5.1.3.
\]

where \( A_{405} \) and \( A_{450} \) are the absorbance values of the solution mixture at 405 and 450 nm respectively. \( \varepsilon \) values represent the molar absorptivities of Ti (IV) and Mo (VI) complexes at the wavelengths specified. 47.87 \times 10^3 and 95.9 \times 10^3 are the factors to convert the concentrations into amounts for Ti (IV) and Mo (VI) respectively.

Thus simultaneous determination of Ti (IV) and Mo (VI) in synthetic mixtures is, therefore, carried out by the following procedure.

**Procedure**

Into a 10ml volumetric flask containing 5 ml of buffer solution (pH 2.0), 1ml of 2-HNHBH (1.0 \times 10^{-2} M) solution and a known aliquot of the synthetic mixture containing Ti (IV) and Mo (VI) are added. The absorbance of the solution is measured at 405 nm and 450 nm against the reagent blank. The amount of Ti (IV) and Mo (VI) is computed from equations 5.1.3. and 5.1.4. respectively. The results are presented in table 5.1.1.
Table 5.1.1
Simultaneous determination of Mo (VI) and Ti (IV) in synthetic mixtures

<table>
<thead>
<tr>
<th>Amount taken (µg/ml)</th>
<th>Amount found* (µg/ml)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo (VI)</td>
<td>Ti (IV)</td>
<td>Mo (VI)</td>
</tr>
<tr>
<td>0.479</td>
<td>3.63</td>
<td>0.472</td>
</tr>
<tr>
<td>0.479</td>
<td>2.42</td>
<td>0.481</td>
</tr>
<tr>
<td>0.479</td>
<td>1.815</td>
<td>0.475</td>
</tr>
<tr>
<td>0.479</td>
<td>1.21</td>
<td>0.470</td>
</tr>
<tr>
<td>0.479</td>
<td>0.605</td>
<td>0.483</td>
</tr>
<tr>
<td>0.479</td>
<td>0.302</td>
<td>0.473</td>
</tr>
<tr>
<td>0.479</td>
<td>0.302</td>
<td>0.482</td>
</tr>
<tr>
<td>0.959</td>
<td>0.302</td>
<td>0.952</td>
</tr>
<tr>
<td>1.918</td>
<td>0.302</td>
<td>1.916</td>
</tr>
<tr>
<td>2.877</td>
<td>0.302</td>
<td>2.884</td>
</tr>
</tbody>
</table>

*Average of seven determinations

Applications

The proposed method is applied to an alloy steel for the simultaneous assay of Ti (IV) and Mo (VI). The alloy steel is brought into solution by adopting the procedure in 3.n. The sample is analyzed by the following procedure.

Procedure

A known aliquot of the alloy sample solution is added to 5 ml of the buffer (pH 2.0) taken in a 10 ml volumetric flask. 1 ml of 2-HNHBH solution (1.0 × 10⁻²M) and 1 ml of 0.1 M oxalate solution [to mask Fe(III)] are then added. The contents are made up to the mark with distilled water. The absorbance of the solution is measured at 375 nm and 470 nm against the reagent blank. The amounts of titanium (IV) and

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molybdenum (VI) are computed from equations 5.1.3. and 5.1.4. respectively. The results are presented in table 5.1.2.

Table 5.1.2.

Simultaneous determination of Mo (VI) and Ti (IV) in alloy sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (%) certified</th>
<th>Composition (%) found *</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo (VI)</td>
<td>Ti (IV)</td>
<td>Mo (VI)</td>
</tr>
<tr>
<td>BAS-387 alloya</td>
<td>5.83</td>
<td>2.95</td>
<td>5.81</td>
</tr>
</tbody>
</table>

* Average of seven determinations.

a) Mo 5.83%; Ti 2.95%; Ni 4.19%; Fe 36%; Cr 12.46%; Al 0.24%; Cu 0.21%; Mn 0.08%; Co 0.32%; C 0.030%.

Conclusions

Titanium (IV) and molybdenum (VI) are associated with each other in many industrially important alloy and steel samples. Hence, their simultaneous assay is important. No direct spectrophotometric determination of Ti(IV) and Mo(IV) is reported in the literature. The present methods is simple, direct, rapid, accurate and can be easily applied for the analysis of Ti (IV) and Mo (VI) in alloy samples.
Section 2: Simultaneous spectrophotometric determination of molybdenum(VI) and copper(II)

Molybdenum (VI) reacts with 2-HNHBH in the pH range of 1.0 to 6.0 to form orange red coloured water soluble complex. The colour intensity is maximum at the pH 2.0 (c.f. section 4.2). The complex shows λ_max at 450 nm. Copper (II) reacts with 2-HNHBH giving yellow coloured water soluble complex in the pH range of 1.0 to 5.0 (c.f. section 4.2) and has absorbance maximum at 430 nm.

Thus, it is clear that both Mo (VI) and Cu (II) react with 2-HNHBH forming water soluble coloured complexes and have maximum absorbance at pH 2.0. It is, therefore, clear that Mo (VI) and Cu (II) can be determined simultaneously with 2-HNHBH spectrophotometrically. The following procedure is adopted for the purpose.

Absorption spectra

The absorption spectra of the following solutions are recorded for selecting the wavelengths for absorbance measurements.

Solution (a)

The absorption spectrum of 2-HNHBH (5.0 \times 10^{-3} \text{ M}) in pH 2.0 is recorded by following the procedure in 3.a and presented in fig.5.1.1a.

Solution (b)

The absorption spectrum of Cu (II)-2-HNHBH complex (5.0 \times 10^{-4} \text{ M}) is recorded by following the procedure in 3.b and presented in fig.5.1.1b.

Solution (c)

The absorption spectrum of Mo (VI) - 2-HNHBH complex (5.0 \times 10^{-4} \text{ M}) is recorded by following the procedure in 3.b and presented in fig.5.1.1c.
Fig. 5.2.1 Absorbance spectra of
a) 2-HNHBH system Vs buffer blank
b) Cu(II)-2-HNHBH system Vs reagent blank
c) Mo(VI)-2-HNHBH Vs reagent blank

$[\text{Cu(II)}] = [\text{Mo(VI)}] = 5 \times 10^{-4} \text{ M; pH 2.0}$

$[2\text{-HNHBH}] = 5 \times 10^{-3} \text{ M}$
From the spectra in fig. 5.2.1., it is clear that Mo(VI) shows absorbance maximum at 450 nm and Cu(II) shows absorbance maximum at 430 nm. It is also noticed that Mo(VI) shows considerable absorbance at 480 nm where Cu(II) shows zero absorbance, and Cu(II) shows higher absorbance at 430 nm than Mo(VI). The absorbance of the solution containing mixture of Cu(II) and Mo(VI) at 430 nm is equal to the sum of the absorbance values due to individual Mo (VI) and Cu (II) species at this wavelength. This suggests that it is possible to carry out a simultaneous spectrophotometric determination of Mo (VI) and Cu (II) using 2-HNHBH by measuring the absorbance of the solution mixtures at 480 nm and 430 nm.

**Applicability of Beer’s law**

To establish whether Beer’s law is applicable to Mo (VI) and Cu (II) at 480 nm and 430 nm, the absorbance measurements for different amounts with any metal ion is made at both these wavelengths (following the procedure in 3.g.). The results are presented in figs. 5.2.2. and 5.2.3.

From the linear plots it is observed that Beer’s law is obeyed for Mo (VI) in the range 0.479-4.479 \( \mu g/ml \) at 480 nm and 0.479-4.479 \( \mu g/ml \) at 430 nm. Cu (II) obeys Beer’s law in the range of 0.112 to 2.233 \( \mu g/ml \) at 430 nm. The molar absorptivities for Mo (VI) are 0.550 ± 0.004 \( \times 10^4 \) \( \text{lit mol}^{-1} \text{cm}^{-1} \) and 0.510 ± 0.004 \( \times 10^4 \) \( \text{lit mol}^{-1} \text{cm}^{-1} \) at 480 nm and 430 nm respectively. The molar absorptivity for Cu(II) at 430 nm is 1.58 ±0.0021 \( \times 10^4 \) \( \text{lit mol}^{-1} \text{cm}^{-1} \). It is also observed that the absorbance at 430 nm is equal to the sum of the absorbance values due to the individual Mo (VI) and Cu (II) species at this wavelength. Hence, simultaneous spectrophotometric determination of Mo (VI) and Cu (II) is carried out.

The absorbance of the solution mixtures containing Mo (VI) and Cu (II) complex species is recorded at 480 nm and 430 nm at pH 2.0. From the absorbance value at 480 nm (where Cu(II) has zero absorbance) the amount of Mo(VI) is computed from the predetermined calibration plot (fig. 5.2.2). The amount of Cu(II) is calculated from the absorbance values measured at 430 nm (\( A_{430} \) nm is obtained after subtracting the absorbance due to Mo(VI) at this wavelength). The absorbance of Mo(VI) at 480 nm is
Fig. 5.2.2  Zero order absorbance Vs amount of Mo(VI)  
\[ pH = 2.0; \]

\[ A_{480} = 0.0684C + 0.0007 \]
\[ A_{430} = 0.0465C + 0.0009 \]

Fig. 5.2.3  Zero order absorbance Vs amount of Cu(II)  
\[ pH = 2.0; \lambda = 430 \text{ nm} \]
1.5 times its absorbance at 430 nm. Therefore, the amount of Cu(II) is computed from the absorbance measured at 430 nm. The following equation is employed to calculate the amounts of Cu(II) at 430 nm.

\[
\text{Cu} = \frac{A_{430} - (A_{480} \times 0.92)}{430 \varepsilon_{\text{Cu}}} \times 63.5 \times 10^3 \ldots \ldots 5.2.1
\]

Where \(A_{430}\) and \(A_{480}\) are the absorbance values of the solution mixtures at 430 and 480 nm respectively. \(430 \varepsilon_{\text{Cu}}\) is the molar absorptivity of Cu(II) at 430 nm. \(63.5 \times 10^3\) is the factor to convert the concentrations of Cu(II) into micro grams. \(A_{480} \times 0.92\) is correction factor to correct for the absorbance due to Mo(VI) at 430 nm.

The simultaneous spectrophotometric determination of Mo(VI) and Cu(II) in synthetic mixtures is, therefore, carried out by the following procedure.

**Procedure**

Into a 10ml volumetric flask containing 5 ml of buffer solution (pH 2.0), 1.0 ml of 2-HNHBH \((5 \times 10^{-3}\text{M})\) solution and a known aliquot of the synthetic mixture containing Cu(II) and Mo (VI) are added. The absorbance of the solution is measured at 430 nm and 480 nm against the reagent blank. The amount of Cu(II) and Mo(VI) is computed from equations 5.2.3. and 5.2.4. respectively. The results are presented in table 5.2.1.
Table 5.2.1.

Simultaneous determination of Mo(VI) and Cu(II) in synthetic mixtures

<table>
<thead>
<tr>
<th>Amount taken (µg/ml)</th>
<th>Amount found* (µg/ml)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(VI)</td>
<td>Cu(II)</td>
<td>Mo(VI)</td>
</tr>
<tr>
<td>0.959</td>
<td>0.317</td>
<td>0.950</td>
</tr>
<tr>
<td>0.959</td>
<td>0.635</td>
<td>0.951</td>
</tr>
<tr>
<td>0.959</td>
<td>0.952</td>
<td>0.962</td>
</tr>
<tr>
<td>0.959</td>
<td>1.270</td>
<td>0.953</td>
</tr>
<tr>
<td>0.959</td>
<td>1.587</td>
<td>0.964</td>
</tr>
<tr>
<td>0.479</td>
<td>0.317</td>
<td>0.482</td>
</tr>
<tr>
<td>1.439</td>
<td>0.317</td>
<td>1.429</td>
</tr>
<tr>
<td>1.918</td>
<td>0.317</td>
<td>1.924</td>
</tr>
</tbody>
</table>

* Average of seven determinations

Applications

The method is applied for the determination of Mo(VI) and Cu(II) in alloy samples. The alloy sample is brought into solution by adopting the procedure in 3.n. Since, no alloy steel containing molybdenum and copper in the ratios required is available, a known amount of Mo(VI) is added to the titanium based alloy sample and the percentages of Mo(VI) and Cu(II) now present are determined by the present method. The certified composition of alloy samples and their composition after the addition of Cu(II) are given underneath the table containing the results (table 5.2.2).

The amount of Mo(VI) and Cu(II) present in the sample are determined by employing the following procedure.
Procedure

A known aliquot of the alloy sample solution is added to 5 ml of the buffer (pH2.0) taken in a 10ml volumetric flask. 1ml of 2-HNHBH (5×10^{-3}M) solution and 1 ml of 0.1 M citrate [to mask Ti(IV)] are then added. The absorbance of the solution is measured at 430 nm and 480 nm against the reagent blank. The amounts of molybdenum (VI) computed from the absorbance measured at 480 nm (referring to its predetermined calibration plot) while the amount of Cu(II) is computed from the equation 5.2.1. The results are presented in table 5.2.2.

Table 5.2.2
Simultaneous determination of Mo(VI) and Cu(II) in alloy samples

<table>
<thead>
<tr>
<th>Alloy sample</th>
<th>Composition (%)</th>
<th>Composition (%)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>certified</td>
<td>Found*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo(VI)</td>
<td>Cu(II)</td>
<td>Mo(VI)</td>
</tr>
<tr>
<td>Titanium based alloy^a</td>
<td>7.00</td>
<td>3.86</td>
<td>6.92</td>
</tr>
</tbody>
</table>

*Average of seven determinations

a) Ni 14.05%; Cu 14.83%; rest Ti

(% composition after adding Mo(VI))

Ni 14.05%; Cu 13.86%; Mo 7.00%; Rest Ti

Conclusions

Mo(VI) and Cu(II) are two industrially important metal ions which are present together in some alloy samples. Hence, their simultaneous determination is of importance, as it enhances the selectivity of the method. No simultaneous spectrophotometric determination of Mo(VI) and Cu(II) id reported in the literature. The present method for their simultaneous assay is simple, direct, rapid, accurate and precise and can be applied for the analysis of Mo(VI) and Cu(II) in alloy samples.
Section 3: Simultaneous spectrophotometric determination of titanium(IV) and copper(II)

Titanium(IV) reacts with 2-HNHBH in the pH range of 1.0 to 4.0 to form brown coloured water soluble complex. The colour intensity is maximum at pH 2.0 (c.f. section 4.2). The complex shows $\lambda_{\text{max}}$ at 405 nm. Copper(II) reacts with 2-HNHBH giving yellow coloured water soluble complex in the pH range of 1.0 to 7.0 and has maximum intensity in the pH 2.0 at 430 nm.

Thus it is clear that both Ti(IV) and Cu(II) reacts with 2-HNHBH forming water soluble coloured complexes and have maximum intensities at pH 2.0. It is, thus, possible to determine Ti(IV) and Cu(II) simultaneously, spectrophotometrically with 2-HNHBH. The following procedure is adopted for the purpose.

Absorption spectra

The absorption spectra of the following solutions are recorded for selecting the wavelengths for absorbance measurements.

Solution (a)

The absorption spectrum of 2-HNHBH ($5 \times 10^{-3}$ M) in pH 2.0 is recorded by following the procedure in 3.a and presented in fig.5.3.1a.

Solution (b)

The absorption spectrum of Ti(IV)-2-HNHBH complex ($5 \times 10^{-4}$ M) is recorded by following the procedure in 3.b. and presented in fig 5.3.1b.
Fig. 5.3.1 Absorption spectra of
a) 2-HNHBH system Vs buffer blank
b) Ti(IV)-2-HNHBH system Vs reagent blank
c) Cu(II)-2-HNHBH Vs reagent blank

\[ [\text{Cu(II)}] = [\text{Ti(VI)}] = 5 \times 10^{-4}\text{ M}; \text{pH 2.0} \]
\[ [2-\text{HNHBH}] = 5 \times 10^{-3}\text{ M} \]
Solution (c)

The absorption spectrum of the Cu(II)-2-HNHBH complex (5×10⁻⁴ M) is recorded by following the procedure in 3.b and presented in fig. 5.3.1b.

From the spectra in fig. 5.3.1, it is clear that Ti(IV) shows absorbance maximum at 405 nm and Cu(II) shows maximum absorption at and beyond 430 nm. It is further noticed that Ti(IV) shows higher absorbance at 405 nm than Cu(II) and less absorbance at 430 nm and vice versa. The absorbance of the solution mixture containing Ti(IV) and Cu(II) either at 405 or 430 nm is found to be equal to the sum of the absorbance values due to individual Ti(IV) and Cu(II) species at these wavelengths. This suggests that it is possible to carry at a simultaneous direct spectrophotometric determination of Ti(IV) and Cu(II) using 2-HNHBH by measuring the absorbance of solution mixtures at 405 nm and 430 nm.

Applicability of Beer’s law

To establish whether Beer’s law is applicable to Ti(IV) and Cu (II) at 405 nm and 430 nm, the absorbance measurements for different amounts with any metal ion is made at both these wavelengths (following procedure in 3.g.). The results are presented in figs. 5.3.2. and 5.3.3.

From the linear plots it is observed that Beer’s law is obeyed for Cu(II) in the range 0.635-6.350 µg/ml at 430 nm and 0.635 to 3.810 µg/ml at 405 nm. Ti (IV) obeys Beer’s law in the range of 0.239-1.916 µg/ml at 405 nm and 0.479 to 1.437 at 430 nm. The molar absorptivities for Cu(II) are 1.58 ± 0.002 ×10⁴ lit mol⁻¹ cm⁻¹ and 1.0 ± 0.002 × 10⁴ lit mol⁻¹ cm⁻¹ respectively at 430nm and 405 nm and similarly, for Ti (IV) they are 1.68 ± 0.002 ×10⁴ lit mol⁻¹ cm⁻¹ and 0.996 ± 0.002 × 10⁴ lit mol⁻¹ cm⁻¹ at 405 and 430 nm respectively.

The absorbance of the solution mixture containing Ti (IV) and Cu(II) complex species is recorded at 405 nm and 430 nm at pH 2.0. From these absorbance
Fig. 5.3.2  Zero order absorbance Vs amount of Ti(IV)  
pH 2.0

\[
A_{\text{abs}} = 0.2541C + 0.0039  
A_{\text{abs}} = 0.2072C + 0.0016
\]

Fig. 5.3.3  Zero order absorbance Vs amount of Cu(II)  
pH = 2.0

\[
A_{\text{abs}} = 0.1699C + 0.0013  
A_{\text{abs}} = 0.1303C + 0.0023
\]
values the amount of Ti(IV) and Cu(II) are calculated using the following simultaneous equations.

\[ A_{405} = \varepsilon_{405} C_{Ti} + \varepsilon_{405} C_{Cu} \]  \hspace{1cm} \text{......5.3.1}
\[ A_{430} = \varepsilon_{430} C_{Ti} + \varepsilon_{430} C_{Cu} \]  \hspace{1cm} \text{......5.3.2}

Converting concentrations into amounts (μg/ml) and solving the equation 5.3.1. and 5.3.2 we get,

\[ \text{Ti (IV)} = \frac{A_{405} \varepsilon_{Ti}^{405} - A_{430} \varepsilon_{Cu}^{405}}{\varepsilon_{405}^{Ti} \varepsilon_{405}^{Cu} - \varepsilon_{430}^{Cu} \varepsilon_{405}^{Ti}} \times 47.9 \times 10^3 \] \hspace{1cm} ...5.3.3.

\[ \text{Cu(II)} = \frac{A_{405} \varepsilon_{Cu}^{405} - A_{430} \varepsilon_{Ti}^{405}}{\varepsilon_{405}^{Ti} \varepsilon_{430}^{Cu} - \varepsilon_{430}^{Cu} \varepsilon_{405}^{Ti}} \times 63.5 \times 10^3 \] \hspace{1cm} ...5.3.4.

where \( A_{405} \) and \( A_{430} \) are the absorbance values of the solution mixture at 405 and 430 nm respectively. \( \varepsilon \) values represent the molar absorptivities of Ti (IV) and Cu(II) complexes at the wavelengths specified. 47.87 \times 10^3 and 63.5 \times 10^3 are the factors to convert the concentrations into amounts for Ti(IV) and Cu(II) respectively.

Thus simultaneous direct spectrophotometric determination of Ti(IV) and Cu(II) in synthetic mixtures is, therefore, carried out by the following procedure.

Procedure

Into a 10ml volumetric flask containing 5 ml of buffer solution (pH 2.0), 1ml of 2-HNHBH (5.0 \times 10^{-3} M) solution and a known aliquot of the synthetic mixture containing Ti(IV) and Cu(II) are added. The absorbance of the solution is measured at 405 nm and 430 nm against the reagent blank. The amount of Ti(IV) and Cu(II) is computed from equations 5.3.3. and 5.3.4. respectively. The results are presented in table 5.3.1.
Table 5.3.1.  
Simultaneous determination of Ti(IV) and Cu(II) in synthetic mixtures

<table>
<thead>
<tr>
<th>Amount taken (µg/ml)</th>
<th>Amount found* (µg/ml)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(IV) Cu(II) Ti(IV) Cu(II) Ti(IV) Cu(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.479 0.635 0.471 0.630 +1.6 +0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.479 1.587 0.475 1.582 +0.83 +0.31</td>
<td></td>
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</tr>
<tr>
<td>0.479 1.905 0.480 1.909 -0.20 -0.20</td>
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<tr>
<td>0.479 2.54 0.482 2.52 -0.62 +0.78</td>
<td></td>
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</tr>
<tr>
<td>0.479 3.175 0.476 3.182 +0.62 -0.22</td>
<td></td>
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</tr>
<tr>
<td>0.479 3.81 0.474 3.74 +1.04 +1.83</td>
<td></td>
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</tr>
<tr>
<td>0.718 1.27 0.710 1.25 +1.11 +1.57</td>
<td></td>
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<tr>
<td>0.958 1.27 0.954 1.28 +0.41 -0.78</td>
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</tr>
<tr>
<td>1.437 1.27 1.434 1.30 +0.20 -2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.916 1.27 1.908 1.26 +0.41 +0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.395 1.27 2.389 1.29 +0.25 -1.57</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Average of seven determinations

Applications

The proposed method is applied for an alloy steel for the simultaneous assay of Ti(VI) and Cu(II). The alloy steel is brought into solution by adopting the procedure in 3.n. The sample is analysed by the following procedure.

Procedure

A known aliquot of the alloy sample solution is added to 5 ml of buffer solution (pH 2.0) taken in a 10 ml volumetric flask. 1 ml of 2-HNHBH (5.0×10⁻³M) solution is then added. The contents are made up to the mark with distilled water. The absorbance of the solution is measured at 405 nm and 430 nm against the reagent blank.
Table 5.3.2.
Simultaneous determination of Ti(IV) and Cu(II) in alloy samples

<table>
<thead>
<tr>
<th>Alloy sample</th>
<th>Composition Certified (%)</th>
<th>Composition Found* (%)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti(IV)</td>
<td>Cu(II)</td>
<td>Ti(IV)</td>
</tr>
<tr>
<td>Titanium based alloy</td>
<td>70.14</td>
<td>14.83</td>
<td>70.04</td>
</tr>
</tbody>
</table>

* Average of seven determinations

a) Ni 15.03%; Cu 14.83%; rest Ti;

Conclusions

Ti(IV) and Cu(II) are two industrially important metal ions which are present together in some alloy samples. Hence, their simultaneous determination is of importance, as it enhances the selectivity of the method. No simultaneous direct spectrophotometric determination of Ti(IV) and Cu(II) is reported in the literature. The present method for their simultaneous assay is simple, direct, accurate and precise and can be applied for the analysis Ti(IV) and Cu(II) in alloy samples.
Section 4: Simultaneous spectrophotometric determination of titanium(IV) and zirconium(IV)

Titanium (IV) reacts with 2-HNHBH in the pH range 1.0 to 6.0 to form brown coloured water soluble complex. The intensity is maximum at the pH 1.0 (c.f. section 4.3). The complex shows $\lambda_{\text{max}}$ at 405 nm. Zirconium(IV) reacts with 2-HNHBH giving yellow coloured water soluble complex in the pH range of 1.0 to 5.0 (c.f. section 4.4) and has absorbance maximum at 415 nm.

Thus, it is clear that both Ti (IV) and Zr(IV) react with 2-HNHBH forming water soluble coloured complexes and have maximum absorbance at pH 1.0. This suggests that it is possible to determine Ti (IV) and Zr (IV) simultaneously, spectrophotometrically with 2-HNHBH. The following procedure is adopted for the purpose.

Absorption spectra

The absorption spectra of the following solutions are recorded selecting the wavelengths for absorbance measurements.

Solution (a)

The absorption spectrum of 2-HNHBH in pH 1.0 is recorded by following the procedure in 3.a and presented in fig.5.4.1.a.

Solution (b)

The absorption spectrum of Ti(IV)-2-HNHBH complex (5.0× 10⁻⁴ M) is recorded by following the procedure in 3.b and presented in fig.5.4.1.b.

Solution (c)

The absorption spectrum of Zr (IV) – 2-HNHBH complex (5.0× 10⁻⁴ M) is recorded by following the procedure in 3.b and presented in fig.5.4.1.c.
Fig. 5.4.1 Absorption spectra of
a) 2-HNHBH system Vs buffer blank
b) Ti(IV)-2-HNHBH system Vs reagent blank
c) Zr(IV)-2-HNHBH Vs reagent blank

\[ [\text{Zr(IV)}] = [\text{Ti(VI)}] = 5 \times 10^{-4} \text{ M}; \text{ pH 1.0} \]
\[ [2-\text{HNHBH}] = 5 \times 10^{-3} \text{ M} \]
From the spectra in fig. 5.4.1., it is clear that Ti (IV) shows maximum absorbance at 405 nm and Zr (IV) shows maximum absorbance at 415 nm. It is further noticed that the absorbance ratio of Ti(IV) to Zr(IV) is maximum at 405 nm while the ratio of Zr(IV) to Ti(IV) is maximum at 438 nm. Also absorbance of the solution mixture containing Ti(IV) or Zr(IV) either at 405 and 438 nm is equal to the sum of the absorbance values due to individual Ti (IV) and Zr(IV) species at these wavelengths. This suggests that it is possible to carry at a simultaneous direct spectrophotometric determination of Ti (IV) and Zr(IV) using 2-HNHBH by measuring the absorbance of the solution mixtures at 405 nm and 438 nm.

Applicability of Beer's law

To establish whether Beer's law is applicable to Zr(IV) and Ti (IV) at 438 nm and 390 nm, the absorbance measurements for various amounts with any metal ion is made at both these wavelengths (following procedure in 3.g.). The results are presented in figs. 5.4.2. and 5.4.3.

From the linear plots it is observed that Beer's law is obeyed for Zr (IV) in the range 0.912-9.12 µg/ml at 438 nm and 0.912 to 3.648 µg/ml at 405 nm. Ti(IV) obeys Beer's law in the range of 0.239 to 1.916 µg/ml at 405 nm and 0.479 to 2.395 µg/ml at 438 nm. The molar absorptivities for Ti (IV) are $0.51 \pm 0.002 \times 10^4$ lit mol$^{-1}$ cm$^{-1}$ and $1.68 \pm 0.002 \times 10^4$ lit mol$^{-1}$ cm$^{-1}$ at 438 nm and 405 nm respectively. The molar absorptivities for Zr (IV) are $0.496 \pm 0.002 \times 10^4$ lit mol$^{-1}$ cm$^{-1}$ and $0.938 \pm 0.002 \times 10^4$ lit mol$^{-1}$ cm$^{-1}$ at 438 nm and 405 nm respectively.

The absorbance of the solution mixture containing Ti (IV) and Zr (IV) complex species is recorded at 405 nm and 438 nm at pH 1.0. From these absorbance values the amount of Ti(IV) and Zr(IV) are calculated using the following simultaneous equations.

\[
\begin{align*}
A_{405} &= Ti \varepsilon_{405} C_{Ti} + Zr \varepsilon_{405} C_{Zr} \quad \ldots..5.4.1 \\
A_{438} &= Ti \varepsilon_{438} C_{Ti} + Zr \varepsilon_{438} C_{Zr} \quad \ldots..5.4.2
\end{align*}
\]
Fig. 5.4.2  Zero order absorbance Vs amount of Zr(IV)  
\[ A_{\text{ex}} = 0.0981C + 0.0011 \] 
\[ A_{\text{em}} = 0.0765C + 0.0011 \]  
\[ \text{pH} 1.0 \]  

Amount of Zr(IV) (pg/ml) 

Fig. 5.4.3  Zero order absorbance Vs amount of Ti(IV)  
\[ A_{\text{ex}} = 0.1193C + 0.00235 \] 
\[ A_{\text{em}} = 0.1748C + 0.00387 \]  
\[ \text{pH} 1.0 \]  

Amount of Ti(IV) (µg/ml)
Converting concentrations into amounts (µg/ml) and solving the equation 5.4.1. and 5.4.2., we get,

\[ Ti \text{ (IV)} = \frac{A_{405}\varepsilon_{438}^{Ti} - A_{438}\varepsilon_{405}^{Zr}}{\varepsilon_{405}^{Ti}\varepsilon_{438}^{Zr} - \varepsilon_{438}^{Ti}\varepsilon_{405}^{Zr}} \times 47.9 \times 10^3 \] ...5.4.2.

\[ Zr \text{ (IV)} = \frac{A_{405}\varepsilon_{405}^{Zr} - A_{438}\varepsilon_{405}^{Ti}}{\varepsilon_{405}^{Ti}\varepsilon_{438}^{Zr} - \varepsilon_{438}^{Ti}\varepsilon_{405}^{Zr}} \times 91.2 \times 10^3 \] ...5.4.2.

where \( A_{405} \) and \( A_{438} \) are the absorbance values of the solution mixture at 405 and 438 nm respectively. \( \varepsilon \) values represent the molar absorptivities of Ti (IV) and Zr (IV) complexes at the wavelengths specified. 47.87 \( \times 10^3 \) and 91.2 \( \times 10^3 \) are the factors to convert the concentrations into amounts for Ti (IV) and Zr (IV) respectively.

Thus simultaneous spectrophotometric determination of Ti (IV) and Zr (IV) in synthetic mixtures is, therefore, carried out by the following procedure.

**Procedure**

Into a 10ml volumetric flask containing 5 ml of buffer solution (pH 1.0), 1ml of 2-HNHBH (5 \( \times 10^{-3} \) M) solution and a known aliquot of the synthetic mixture containing Ti (IV) and Zr (IV) are added. The absorbance of the solution is measured at 405 nm and 438 nm against the reagent blank. The amount of Ti (IV) and Zr (IV) is computed from equations 5.4.3. and 5.4.4. respectively. The results are presented in table 5.4.1.
Table 5.4.1.
Simultaneous determination of Zr(IV) and Ti(IV) in synthetic mixtures

<table>
<thead>
<tr>
<th>Amount taken (µg/ml)</th>
<th>Amount found* (µg/ml)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(IV)</td>
<td>Ti(IV)</td>
<td>Zr(IV)</td>
</tr>
<tr>
<td>0.912</td>
<td>2.395</td>
<td>0.908</td>
</tr>
<tr>
<td>0.912</td>
<td>1.916</td>
<td>0.918</td>
</tr>
<tr>
<td>0.912</td>
<td>0.718</td>
<td>0.902</td>
</tr>
<tr>
<td>0.912</td>
<td>0.958</td>
<td>0.906</td>
</tr>
<tr>
<td>0.912</td>
<td>0.479</td>
<td>0.916</td>
</tr>
<tr>
<td>1.824</td>
<td>0.479</td>
<td>1.814</td>
</tr>
<tr>
<td>3.648</td>
<td>0.479</td>
<td>3.634</td>
</tr>
<tr>
<td>5.472</td>
<td>0.479</td>
<td>5.422</td>
</tr>
<tr>
<td>7.296</td>
<td>0.479</td>
<td>7.224</td>
</tr>
<tr>
<td>9.12</td>
<td>0.479</td>
<td>9.2</td>
</tr>
</tbody>
</table>

* Average of seven determinations

Applications

The proposed method is applied to an alloy steel for the simultaneous assay of Ti(IV) and Zr(IV). The alloy steel is brought into solution by adopting the procedure in 3.n. The sample is analyzed by the following procedure.

Procedure

A known aliquot of the alloy sample solution is added to 5 ml of the buffer (pH 1.0) taken in a 10 ml volumetric flask. 1 ml of 2-HNHBH solution (5×10⁻³M) is then added. The contents are made up to the mark with distilled water. The absorbance of the solution is measured at 405 nm and 438 nm against the reagent blank. The amounts of Ti(IV) and Zr(IV) are computed from equations 5.4.3. and 5.4.4. respectively. The results are presented in table 5.4.2.
Table 5.4.2.
Simultaneous determination of Zr(IV) and Ti(IV) in alloy sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (%) certified</th>
<th>Composition (%) found*</th>
<th>Relative error(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zr(IV)</td>
<td>Ti(IV)</td>
<td>Zr(IV)</td>
</tr>
<tr>
<td>Titanium based Alloy (Beta C)</td>
<td>4.0</td>
<td>75.0</td>
<td>3.96</td>
</tr>
</tbody>
</table>

* Average of seven determinations

Ti 75%; Al 3.0%; V 8%; Cr 6%; Zr 4%; Mo 4%;

Conclusions

Zirconium(IV) and titanium(IV) are associated with each other in many industrially important alloy steel samples. Hence, their simultaneous assay is important as it increases the selectivity of the method. Further no method for the simultaneous direct spectrophotometric determination of Ti(IV) and Zr(IV) is reported in the literature. The present is simple, direct, rapid, accurate and easily applied for the analysis of Ti(IV) and Zr(IV) in alloy samples.
Section 5: Simultaneous spectrophotometric determination of titanium(IV) and thorium(IV)

Titanium (IV) reacts with 2-HNHBH in the pH range 1.0 to 6.0 to form brown coloured water soluble complex. The intensity is maximum at the pH 1.0 (c.f. section 4.3). The complex shows $\lambda_{\text{max}}$ at 405 nm. Thorium(IV) reacts with 2-HNHBH giving yellow coloured water soluble complex in the pH range of 1.0 to 5.0 and has absorbance maximum at 425 nm.

Thus, it is clear that both Ti (IV) and Th(IV) react with 2-HNHBH forming water soluble coloured complexes and have maximum absorbance at pH 1.0. It is, therefore, possible to develop a direct simultaneous spectrophotometric method for Ti(IV) and Th(IV) using 2- HNHBH. The following procedure is adopted for the purpose.

Absorption spectra

The absorption spectra of the following solutions are recorded selecting the wavelengths for absorbance measurements.

Solution (a)

The absorption spectrum of 2-HNHBH in pH 1.0 is recorded by following the procedure in 3.a and presented in fig.5.5.1.a.

Solution (b)

The absorption spectrum of Ti(IV)-2-HNHBH complex ($5.0 \times 10^{-4}$ M) is recorded by following the procedure in 3.b and presented in fig.5.5.1.b.
Fig. 5.1 Absorption spectra of
a) 2-HNHBH system Vs buffer blank
b) Ti(IV)-2-HNHBH system Vs reagent blank
c) Th(IV)-2-HNHBH Vs reagent blank
[Th(IV)] = [Ti(VI)] = 5×10^{-4} M; pH 1.0
[2-HNHBH] = 5×10^{-3} M
Solution (c)

The absorption spectrum of Th (IV) – 2-HNHBH complex (5.0× 10^4 M) is recorded by following the procedure in 3.b and presented in fig.5.5.1.c.

From the spectra in fig. 5.5.1.c, it is clear that Ti (IV) shows maximum absorbance at 405 nm and Th (IV) shows maximum absorbance at 425 nm. It is also noticed that the absorbance ratio of Ti(IV) to Zr(IV) at 390 nm is maximum while the absorbance ratio of Zr(IV) to Ti(IV) is maximum at 438 nm. Further absorbance of the solution mixture containing Ti(IV) and Th(IV) either at 390 or 438 nm is equal to the sum of the absorbance values due to individual Ti (IV) and Th(IV) species at these wavelengths. This suggests that it is possible to carry at a simultaneous spectrophotometric determination of Ti(IV) and Th(IV) using 2-HNHBH by measuring the absorbance of the solution mixtures at 390 nm and 438 nm.

Applicability of Beer’s law

To establish whether Beer’s law is applicable to Th(IV) and Ti (IV) at 438 nm and 390 nm, the absorbance measurements with any metal ion is made at both these wavelengths (following procedure in 3.g.). The results are presented in figs. 5.5.2. and 5.5.3.

From the linear plots it is observed that Beer’s law is obeyed for Th (IV) in the range 1.16-9.28 µg/ml at 438 nm and 1.16 to 6.96 µg/ml at 390 nm. Ti obeys Beer’s law in the range of 0.479 to 2.395 µg/ml at 405 nm and 0.239 to 1.437 µg/ml at 438 nm. The molar absorptivities for Ti (IV) are 0.51± 0.002 ×10^4 lit mol⁻¹ cm⁻¹ and 0.64± 0.002 × 10^4 lit mol⁻¹ cm⁻¹ at 438nm and 390 nm respectively. The molar absorptivities for Th (IV) are 1.14 ± 0.002 ×10^4 lit mol⁻¹ cm⁻¹ and 0.408 ± 0.002 × 10^4 lit mol⁻¹ cm⁻¹ at 438nm and 390 nm respectively.

The absorbance of the solution mixture containing Ti (IV) and Th (IV) complex species is recorded at 390 nm and 438 nm at pH 1.0. From these absorbance
Fig. 5.5.2 Zero order absorbance Vs amount of Ti(IV) 

pH 1.0

Fig. 5.5.3 Zero order absorbance Vs amount of Th(IV) 

pH 1.0
values the amount of Ti(II) and Th(IV) are calculated using the following simultaneous equations.

\[
A_{390} = \frac{\text{Ti} \cdot \varepsilon_{390} \cdot C_{\text{Ti}} + \text{Th} \cdot \varepsilon_{390} \cdot C_{\text{Th}}}{\varepsilon_{390} \cdot C_{\text{Th}}} 
\]

\[
A_{438} = \frac{\text{Ti} \cdot \varepsilon_{438} \cdot C_{\text{Ti}} + \text{Th} \cdot \varepsilon_{438} \cdot C_{\text{Th}}}{\varepsilon_{438} \cdot C_{\text{Th}}} 
\]

Converting concentrations into amounts (μg/ml) and solving the equations 5.5.1. and 5.5.2., we get,

\[
\text{Ti(IV)} = \frac{A_{390} \cdot \varepsilon_{438}^{\text{Ti}} - A_{438} \cdot \varepsilon_{390}^{\text{Th}}}{\varepsilon_{390}^{\text{Ti}} \cdot \varepsilon_{438}^{\text{Th}} - \varepsilon_{438}^{\text{Th}} \cdot \varepsilon_{390}^{\text{Ti}}} \times 47.9 \times 10^3
\]

\[
\text{Th(IV)} = \frac{A_{390} \cdot \varepsilon_{438}^{\text{Th}} - A_{438} \cdot \varepsilon_{390}^{\text{Ti}}}{\varepsilon_{390}^{\text{Th}} \cdot \varepsilon_{438}^{\text{Th}} - \varepsilon_{438}^{\text{Th}} \cdot \varepsilon_{390}^{\text{Th}}} \times 232 \times 10^3
\]

where \( A_{390} \) and \( A_{438} \) are the absorbance values of the solution mixture at 390 and 438 nm respectively. \( \varepsilon \) values represent the molar absorptivities of Ti (IV) and Th(VI) complexes at the wavelengths specified. 47.87 \( \times 10^3 \) and 232 \( \times 10^3 \) are the factors to convert the concentrations into amounts for Ti (IV) and Th(IV) respectively.

Thus simultaneous spectrophotometric determination of Ti (IV) and Th (IV) in synthetic mixtures is, carried out by the following procedure.

**Procedure**

Into a 10ml volumetric flask containing 5 ml of buffer solution (pH 1.0), 1ml of 2-HNHBH \( (5 \times 10^{-3} \text{ M}) \) solution and a known aliquot of the synthetic mixture containing Ti (IV) and Th (IV) are added. The absorbance of the solution is measured at 390 nm and 438 nm against the reagent blank. The amount of Ti (IV) and Th (IV) is computed from equations 5.5.3. and 5.5.4. respectively. The results are presented in table 5.5.1.
Table 5.5.1.  
Simultaneous determination of Th (IV) and Ti(IV) in synthetic mixtures

<table>
<thead>
<tr>
<th>Amount taken (µg/ml)</th>
<th>Amount found* (µg/ml)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Th(IV)</td>
<td>Ti(IV)</td>
</tr>
<tr>
<td>2.32</td>
<td>2.395</td>
<td>2.30</td>
</tr>
<tr>
<td>2.32</td>
<td>1.916</td>
<td>2.29</td>
</tr>
<tr>
<td>2.32</td>
<td>0.958</td>
<td>2.33</td>
</tr>
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<td>2.32</td>
<td>0.718</td>
<td>2.37</td>
</tr>
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<td>2.32</td>
<td>0.249</td>
<td>2.31</td>
</tr>
<tr>
<td>2.32</td>
<td>0.479</td>
<td>2.28</td>
</tr>
<tr>
<td>4.64</td>
<td>0.479</td>
<td>4.6</td>
</tr>
<tr>
<td>6.96</td>
<td>0.479</td>
<td>6.92</td>
</tr>
<tr>
<td>9.28</td>
<td>0.479</td>
<td>9.32</td>
</tr>
<tr>
<td>11.6</td>
<td>0.479</td>
<td>11.4</td>
</tr>
</tbody>
</table>

* Average of seven determinations

Applications

The proposed method is applied to an alloy steel for the simultaneous assay of Ti(IV) and Th(IV). The alloy steel is brought into solution by adopting the procedure in 3.n. The sample is analysed by the following procedure.

Procedure

A known aliquot of the alloy sample solution is added to 5 ml of the buffer (pH 1.0) taken in a 10 ml volumetric flask. 1 ml of 2-HNHBH solution (5×10^{-3}M) is then added. The contents are made up to the mark with distilled water. The absorbance of the solution is measured at 390 nm and 438 nm against the reagent blank. The amounts of Ti(IV) and Th(IV) are computed from equations 5.5.3. and 5.5.4. respectively. The results are presented in table 5.5.2.
Table 5.5.2

Simultaneous determination of Ti(IV) and Th(IV) in alloy sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (%) certified</th>
<th>Composition (%) found*</th>
<th>Relative error(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(IV)</td>
<td>Th(IV)</td>
<td>Ti(IV)</td>
<td>Th(IV)</td>
</tr>
<tr>
<td>Magnesium based</td>
<td>6.0</td>
<td>2.5</td>
<td>5.94</td>
</tr>
<tr>
<td>alloy</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Average of seven determinations

Th 3.0%; Zr 0.7 %; Rest Mg

(%) composition after adding Ti(IV)

Th 2.86%; Ti 4.76%; Zr 0.66%; Rest Mg

Conclusions

Thorium(IV) and titanium(IV) are associated with each other in many industrially important alloy steel samples. Hence, their simultaneous assay has a potentiality. Further it is seen from survey of the literature that no simultaneous direct spectrophotometric method for the assay of Th(IV) and Ti(IV) is reported in the literature. The present method is simple, direct, rapid, accurate and easily applied for the analysis of Ti(IV) and Th(IV) in alloy samples.