Chapter – 10

SIMULTANEOUS DERIVATIVE SPECTROPHOTOMETRIC METHODS
Section (i): An introduction to Simultaneous spectrophotometric determination of metal ions

A great number of spectrophotometric methods are reported in the literature for the determination of almost all metal ions in the periodic table. The two important characteristic features of a spectrophotometric method are sensitivity and specificity or selectivity. Sensitive methods are now a common feature for every metal ion.

A method is said to be selective if it is capable of determining only one metal ion in presence of many others. However, there exist few selective methods. On the other hand it is possible to make a method selective by controlling certain conditions such as oxidation state of the metal ion, pH and the temperature and by using suitable masking agents. Such methods are called selective methods.

The degree of selectivity of a method is dependent on the complexity of the material or the sample being analyzed. In the world of ever increasing technological progress, the modern analytical chemists are confronted with the analysis of materials of more and more complex in nature. In many cases the simultaneous presence of other element is in face a potential cause of interference whenever quantitative determinations of two or more metal ions are carried out. In such cases a simultaneous determination of two or more metal ions enhances the selectivity of the method to greater extent. Therefore, in order to achieve greater degree of selectivity, the emphasis is being laid to develop direct spectrophotometric and derivative spectrophotometric procedures for the simultaneous determination of two or more metal ions when present in admixture. Simultaneous spectrophotometric analysis eliminates wavelength independent matrix
system effect and permits the analysis of two or more components in a system. It also saves the sample, time and thereby enhances the speed of analysis.

Form this point of view spectrophotometric methods for simultaneous determination of metal ions is of immense value and is receiving the attention of many chemists in recent times. Moreover, spectrophotometric and derivative spectrophotometric methods/procedures for the simultaneous determination of two metal ions are in frequently reported in the literature. Hence, the author has developed spectrophotometric methods for the simultaneous determination of two metal ions when present in admixture with each other in several biological samples. The results are presented in this chapter.

However, before this, a brief account of the theoretical aspects of the simultaneous procedures is presented here under.

**Principles of multicomponent spectrophotometric analysis**

If a system containing several absorbing components follows the principle of additive of absorbance’s, i.e, the absorbance of the system is equal to the sum of the absorbance’s of all individual components at a particular wavelength, and if no natural interaction takes place between them, then

$$A_j = \sum_{i=1}^{n} \varepsilon_i C_i \lambda_j$$

where $\varepsilon$ is the molar absorptivity of the component ‘i’ at the wavelength ‘J’ and ‘I’ is the path length.
The additive of absorbance's is easily tested by calculation of absorbance's for mixtures of standard solutions containing known analyze concentrations. The determination of a mixture comprising of several absorbing components in solution is carried out by measuring the absorbance at selected wavelengths and solving a set of simultaneous equations of the type

\[ A_j = \varepsilon_1 C_1 + \varepsilon_2 C_2 + \ldots + \varepsilon_n C_n \lambda_j \]

The accuracy and precision of the calculations is dependent on the number of components present and the selection of suitable wavelengths. At the wavelength selected, always one component absorbs strongly, whereas the other components absorb less intensely.

\[ \varepsilon_{ij} = \varepsilon_1 >> \varepsilon_2 \varepsilon_3 \varepsilon_4 \]

The molar absorptivity of all the components at the selected wavelength are previously determined from solutions of the pure components under the same conditions as for the mixture.

The validity of Beer's law for single component need not be maintained for their mixture. Even if the Beer's law is not obeyed for one component of the mixture, the sum of the absorbance's will still be correct for mixtures with a constant concentration of such a component.

The precision and accuracy of the calculated results depends on the number of unknown components in the mixture. The error of the resulting data considerably increases if more than four absorbing species in unknown concentrations are to be determined.
The set of equations containing 'T' unknowns is solved by the familiar elimination procedures or with the aid of determinants but computer procedures are usually used if more than two absorbing components are to be determined.

**Two component analysis**

For a system containing two absorbing species 1 and 2, the absorbance of the systems at the selected wavelengths (\(\lambda_1\) and \(\lambda_2\)) i.e. \(A_{\lambda_1}\) and \(A_{\lambda_2}\) are given by the following equation.

\[
A_{\lambda_1} = \varepsilon_{\lambda_1}^1 C_1 + \varepsilon_{\lambda_1}^2 C_2 \quad \text{...10.1}
\]

\[
A_{\lambda_2} = \varepsilon_{\lambda_2}^1 C_1 + \varepsilon_{\lambda_2}^2 C_2 \quad \text{...10.2}
\]

Solving the equations (1) and (2) we get,

\[
C_1 = \frac{A_{\lambda_1} \varepsilon_{\lambda_2}^2 - A_{\lambda_2} \varepsilon_{\lambda_1}^2}{\varepsilon_{\lambda_1}^1 \varepsilon_{\lambda_2}^2 - \varepsilon_{\lambda_1}^2 \varepsilon_{\lambda_2}^1} \quad \text{...10.3}
\]

\[
C_2 = \frac{A_{\lambda_2} \varepsilon_{\lambda_1}^1 - A_{\lambda_1} \varepsilon_{\lambda_2}^1}{\varepsilon_{\lambda_1}^1 \varepsilon_{\lambda_2}^2 - \varepsilon_{\lambda_1}^2 \varepsilon_{\lambda_2}^1} \quad \text{...10.4}
\]

Where \(C_1\) and \(C_2\) are the concentrations of analytes 1 and 2, \(\varepsilon_{\lambda_1}^1, \varepsilon_{\lambda_1}^2, \varepsilon_{\lambda_2}^1, \varepsilon_{\lambda_2}^2\) are the molar absorptivity of the components denoted by superscripts 1 and 2 at the wavelengths \(\lambda_1\) and \(\lambda_2\) respectively.
Section (ii): Review of derivative methods for the simultaneous spectrophotometric
determination of metal ions

The direct spectrophotometric determinations of metal ions in multicomponent systems are often complicated by interferences from the formulation matrix and spectral overlapping. Such interferences have been avoided in many ways, such as solving two simultaneous equations\(^1\) or using absorbance ratios at certain wavelengths\(^2\text{-}^4\).

However, during the application of these methods\(^1\text{-}^4\), the presence of spectral interferences or spectral overlap would certainly lead to erroneous results\(^5\). Other approaches aimed at solving this problem have been employed including pH induced differential spectrophotometric\(^6\), least squares\(^7\) and orthogonal function\(^5\text{-}^7\text{-}^8\) methods.

Derivative spectrophotometry is a useful means of resolving two overlapping spectra and eliminating matrix interferences in the assay of two component mixtures using the zero-crossing technique\(^9\text{-}^{11}\). In the absence of a zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture\(^12\). The latter method is based on criteria for selecting the optimum working wavelengths\(^2\). In addition, the component being determined should make a reasonable contribution to the total derivative reading of the mixture at the selective wavelengths.

Derivative spectrophotometric analysis of two-component mixtures is also carried out without the need to solve simultaneous equations. The compensation method\(^13\) is also used for the purpose. It is a non-mathematical method for detection and elimination of unwanted absorption during photometric analysis.

However, only few references are available in the literature on the determination of mixtures of metal ions by derivative spectrophotometry.
Jiang Chogqui et al. established first derivative spectrophotometric method for the simultaneous determination of cobalt and nickel. A second derivative spectrophotometric method was proposed by Jimenez et al. for the simultaneous determination of cobalt and vanadium in alloy steels.

Wang et al. reported a first derivative spectrophotometric method for the simultaneous determination of Fe(III) and Cu(III). A second derivative spectrophotometric method was developed for the nickel and vanadium determination in petroleum and petroleum residues by Wang et al. using the second derivative spectrophotometry.

Bermejo-Barreta et al. described the application of derivative spectrophotometry to the simultaneous determination of Cu(II) and Co(II) without solving the simultaneous equations. Zhenzhuzi et al. determined chromium and manganese simultaneously by second derivative spectrophotometry. Cu(II) and Zn(II) were determined continuously by Li Huamin and Yan Junfeng using fourth derivative spectrophotometry.

Kuroda et al. reported the simultaneous determination of U(VI) and Th(IV) by first derivative spectrophotometric method has been developed for the simultaneous determination of U(VI) and Th(IV) by Ramesh et al. A simultaneous first derivative spectrophotometric determination of Cu(II) and Co(II) was carried out by Vereda et al. Pd(II) and Co(II) were determined simultaneously by derivative spectrophotometry by Peruez et al.

Simultaneous determination of Ni(II), Zn(II) and Cu(II) by second derivative spectrophotometry was reported by Gallardo Maelgarejo et al. Perikov et al. reported simultaneous extraction spectrophotometric determination of iron, nickel, cobalt, zinc and
cadmium. Recently, Fernández-Alba et al. presented simultaneous second derivative spectrophotometric determination of Mn and Cu.

Simultaneous spectrophotometric determination of zinc(II) and nickel(II) was reported by Blanco et al. Wang et al. reported simultaneous third derivative spectrophotometric determination of Cu(II) and Ni(II) in iron-alloys and aluminum alloys. Costa et al. reported determination of nickel and iron in cobalt base alloy by simultaneous method. Sayed et al. reported simultaneous first derivative spectrophotometric determination of Fe(III) and Mo(VI) in Co-Cr and Ni-Cr alloys. Ines et al. reported Cu(II) and Fe(II) by second derivative simultaneous spectrophotometry using mixtures of ligands. Simultaneous determination of Cu and Fe was reported by Baraj. Recently, simultaneous first and second derivative spectrophotometric determination of Ni(II) and Cu(II) using diacetylmonoxime benzoylhydrazone (DMBH) was carried out in our laboratory. Ni(II) and Cu(II) were also determined by simultaneous second derivative spectrophotometry employing diacetylmonoxime isonicotinoylhydrazone (DMIH).

Simultaneous determination of Cd (II) and Hg (II) was reported by Elham et al. Simultaneous spectrophotometric determination of Cu (II) and Ni (II) was reported by Prasad et al. Non-extractive trace level simultaneous determination of Hg(II) and Zn II) in environmental samples was reported by Agnihotri et al. Simultaneous first derivative determination of Cu(II) and Ni(II) was reported by Prasad et al. Simultaneous determination of Co (II) and Pd (II) in alloy samples was reported by Bagherian.
Simultaneous first derivative spectrophotometric determination of Ni(II) and Cu(II) in alloys was reported by Chandrasekhar$^{43}$ et.al. Derivative Spectrophotometric determination of Ni(II) and Cu(II) in alloys was proposed by Chandrasekhar$^{44}$ et.al. Simultaneous second derivative spectrophotometric determination of Ni(II) and Cu(II) was reported by Chandrasekhar$^{40}$ et. al. Simultaneous second derivative spectrophotometric determination of Ni(II) and Cu(II) in alloys was also reported by Chandrasekhar$^{46}$ et. al. using diacetylmonoxime benzoylhydrazone.
Section (iii): Simultaneous second derivative spectrophotometric determination of copper(II) and cobalt(II) using 2-acetylpyridine 4-methyl-3-thiosemicarbazone (APMT)

The second derivative spectra of copper (II) and cobalt(II) complexes with 2-acetylpyridine -4-methyl-3-thiosemicarbazone (APMT) (Section (i) and Section (ii) of chapter 9) show maximum amplitude at 430 nm (peak) and at 407 nm (valley) for copper(II), and 455 nm (peak) for cobalt(II) respectively. The derivative amplitude increases proportionately with the concentration of the metal ions concerned at the wavelengths specified. Investigations were therefore carried out to explore the possibility of simultaneous second derivative spectrophotometric determination of copper (II) and cobalt (II).

Second derivative spectra of Cu (II) and Co (II) complexes

The second derivative spectra of Cu (II) and Co (II) were recorded at pH 6.0 by employing the procedure given in 2.iv.a.

From the spectra in Fig 10.iii.a it is noticed that copper (II) shows maximum amplitudes at 430 nm and cobalt (II) at 455 nm. At 435 nm cobalt has zero amplitude (zero cross). Further at this wavelength copper (II) has approximately maximum amplitude. Copper has a zero cross at 460 nm while at this wavelength Co (II) has appreciable amplitude and proportional to the concentration of the metal ion.

Hence, a simultaneous second derivative spectrophotometric determination of Cu (II) and Co (II) was carried out by measuring the peak amplitudes at 435 nm and 460 nm respectively. Typical spectra are shown in Fig 10.iii.a.
Fig: 10.iii.a  Second derivative spectra of a. Cu(II) – APMT system; b. Co(II) – APMT system

- [Cu(II)] = 2 x 10^{-5} M
- [Co(II)] = 2 x 10^{-5} M
- [APMT] = 6 x 10^{-4} M
- pH = 6.0
Calibration plots

To determine the linear relationship between the derivative amplitudes and concentration of Cu (II) and Co (II) ions at 435 nm and 450 nm respectively, individual calibration plots were constructed. The plots are shown in Figs 10.iii.b and 10.iii.c.

The plots are linear and obey the following relationships

\[ A_{435} = 0.0677 \, C - 0.001 \]

and

\[ A_{460} = 0.0659 \, C + 0 \]

for Cu(II) and Co (II) respectively. The amplitude is proportional to the metal ion concentration in the range of 0.15 – 2.0 µg/ml of Cu (II) and 0.13 – 2.0 µg/ml of Co (II) at 435 nm and 460 nm respectively.

The simultaneous second derivative spectrophotometric determination of Cu (II) and Co (II) in the synthetic mixtures was carried out by adopting the procedure given below

Procedure

To a known aliquot of the synthetic mixture of Cu(II) and Co(II) taken in a 25-ml volumetric flask, 10 ml buffer solutions (pH 6.0), and 1ml of APMT (1×10^{-2} M) solution were added. The contents of the flask were made upto the mark with distilled water and the second derivative spectrum were recorded and presented in Figs 10.iii.b and 10.iii.c. The derivative amplitudes at 435 nm and 460 nm were measured and the amount of Cu (II) and Co (II) were computed from the predetermined calibration plots. The results are presented in Table 10.iii.1.
Fig: 10.iii.b  Second derivative Amplitude Vs amount of Cu (II) µg/ml

$A_{415} = 0.0677C - 0.001$

pH = 6.0

$[APMT] = 6 \times 10^{-4}$ M
Fig: 10.iii.c  
Second derivative Amplitude Vs amount of Co (II) µg/ml

\[ A_{460} = 0.0659C \]

\[ \text{pH} = 6.0 \]

\[ [\text{APMT}] = 6 \times 10^{-4} \text{ M} \]
The present method does not involve either solving of simultaneous equations or computation of the amplitude of a particular species. Further, it has been successfully employed for the accurate determination of copper (II) and cobalt (II).

Table 10.iii.1
Simultaneous second derivative determination of Cu (II) and Co (II) in synthesis mixtures*

<table>
<thead>
<tr>
<th>Amount in (µg/ml)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Taken</strong></td>
<td><strong>Found</strong></td>
</tr>
<tr>
<td>1.524 0.472</td>
<td>1.524 0.481</td>
</tr>
<tr>
<td>1.524 0.708</td>
<td>1.530 0.706</td>
</tr>
<tr>
<td>1.524 0.944</td>
<td>1.546 0.945</td>
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<tr>
<td>1.524 1.180</td>
<td>1.520 1.200</td>
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<tr>
<td>1.524 1.416</td>
<td>1.506 1.462</td>
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<tr>
<td>1.524 1.652</td>
<td>1.501 1.690</td>
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<tr>
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<td>1.524 2.164</td>
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<tr>
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<td>0.763 1.446</td>
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<td>1.061 1.399</td>
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<td>2.086 1.416</td>
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<td>2.286 1.416</td>
<td>2.302 1.429</td>
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* Average of five determinations.
References


