Chapter-I

INTRODUCTION

AND

OBJECTIVES
Section-1 Introduction to simultaneous spectrophotometric derivative

Spectrophotometric methods:

Analytical chemistry is the study of matter in order to reveal its composition, structure and extent. Because these are fundamental in just about every chemical inquiry, analytical chemistry is used to obtain information, insure safety and solve problems in many different chemical areas, and is essential in both theoretical and applied chemistry. Analytical chemistry is the art and science of determining what matter is and how much of it exists.

Qualitative approach that was focused on determining what elements and compounds were present and a quantitative approach that aimed to establish the precise amount of an element or compound in a given sample. These qualitative approaches to analytical chemistry can be applied to materials in a variety of fields, including the food and beverage industry, the pharmaceutical industry. Synthetic materials such as polymers and natural materials such as minerals and water samples. As the field grew, analytical chemistry also broadened to embrace applications of its techniques in forensics.

In the last four decades, research on new methods for the trace metal analysis has grown multidimensionally with the introduction of several new metallurgical products of precise compositions. Today in analytical chemistry use a wide variety of technique in their analysis, including some involving robotics, digital microscopes, a Fourier transform infrared spectrophotometers, chip-based technology and chemometrics, titrimetry, chromatography, spectrometry, polarography, neutron activation analysis atomic absorption spectrophotometry, ICP-atomic emission spectrometry, etc.. Among them spectrophotometric methods occupy special position.

The use of spectrophotometers spans various scientific fields, such as physics, chemistry, biochemistry and molecular biology. U.V. visible spectrophotometry is a versatile technique for the analysis of inorganic and organic materials. 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, but selective methods are very few.

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 temperature and by using suitable masking agents. Such methods are termed ‘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 high technological progress, the modern analytical chemist is confronted with the analysis of materials of more and more complex nature. In many cases the simultaneous determination of two or more metal ions enhances the selectivity of the method to a greater extent. Simultaneous spectrophotometric analysis eliminates wavelength independent matrix system effect as well as permits the analysis of two or more component systems. It also saves the sample, time and thereby enhances the speed of analysis.

From this point of view spectrophotometric method for the simultaneous determination of metal ions is of immense value and is receiving the attention of many chemists in recent times. The simultaneous determination of two or more metal ions or organic species can be made using zero order or derivative spectrophotometry. As the author interested in simultaneous determination of metal ions, a brief account of the theoretical aspects of the simultaneous procedures involving zero order and derivative spectrophotometry are presented below.

**Principles of multicomponent spectrometric analysis:**

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

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

Where \( \varepsilon_i \) is the molar absorptivity of the component ‘i’ at the wavelength \( j \) and “L” is the path length.

The additivity of absorbance is easily tested by calculation of absorbance for mixtures of standard solutions containing known analyte 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 equation of the type

\[ A_j = \varepsilon_1 C + \varepsilon_2 C + \ldots \ldots \ldots \varepsilon_n C \lambda_j \]

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 other components absorb less intensely.

\[ \varepsilon_1 \gg \varepsilon_2 \gg \varepsilon_3 \gg \varepsilon_4 \]

The molar absorptivities 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 components 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 absorbances still is 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 ‘i’ 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 (λ₁ and λ₂) i.e. A₁ and A₂ are given by the following equations

\[ A_{\lambda 1} = \varepsilon_{\lambda 1} C_1 + \varepsilon_{\lambda 1} C_2 \quad \ldots \quad (1) \]

\[ A_{\lambda 2} = \varepsilon_{\lambda 2} C_1 + \varepsilon_{\lambda 2} C_2 \quad \ldots \quad (2) \]

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

\[ C_1 = \frac{A_{\lambda 1} \varepsilon_{\lambda 2} - A_{\lambda 2} \varepsilon_{\lambda 1}}{\varepsilon_{\lambda 1} \varepsilon_{\lambda 2} - \varepsilon_{\lambda 1} \varepsilon_{\lambda 2}} \quad \ldots \quad (3) \]

\[ C_2 = \frac{A_{\lambda 2} \varepsilon_{\lambda 1} - A_{\lambda 1} \varepsilon_{\lambda 2}}{\varepsilon_{\lambda 1} \varepsilon_{\lambda 2} - \varepsilon_{\lambda 1} \varepsilon_{\lambda 2}} \quad \ldots \quad (4) \]

Where \( C_1 \) and \( C_2 \) are the concentrations of analytes 1 and 2, \( \varepsilon_{\lambda 1}, \varepsilon_{\lambda 1}, \varepsilon_{\lambda 1} \) and \( \varepsilon_{\lambda 2} \) are the molar absorptivities of the components denoted by superscripts 1 and 2 at the wavelength \( \lambda_1 \) and \( \lambda_2 \) respectively.
As seen above, this requires solving of simultaneous equations. As the number of components in a mixture increases the accuracy decreases. The derivative spectrophotometry enables the simultaneous determination of two or more components without the need of solving simultaneous equations.

**Derivative spectrophotometry and its applications**

**Introduction:**

The derivative method in UV -- visible and IR spectrophotometry was introduced in 1953\(^1\)\(^-\)\(^3\). Derivative spectrophotometry has only recently become a generally applied analytical method, since the rapid progress in the technology of microcomputers has made it possible to directly present the first, the second and higher order derivative spectra.

The great interest towards derivative spectrophotometry (DS) is due to the increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences\(^4\)\(^-\)\(^6\). Because of these characteristics, the processes of isolation and preconcentration of active components usually required in qualitative and quantitative spectrophotometric procedures applied in the analysis of complex systems is completely avoided.

The conceptual simplicity, relatively quick and easy realization, increased selectively in the analysis in the analysis of minor components are the main reasons why the interest in DS is constantly growing for practical application, as well as for the development of spectrophotometers with integrated computers and accompanying software for producing derivative spectra of different orders. As a result, a great number of papers dealing both with the theoretical aspects of the derivative technique connected with the appropriate numerical analysis and with detailed critical analysis of derivative techniques of certain order have appeared. These papers also describe the application of DS in different fields, e.g., clinical, pharmaceutical, biochemical and environmental analyses, especially of drugs, food and multi
component organic and inorganic mixtures. General analytical applications of UV-visible
derivative spectrophotometry have been reviewed for the period till 1993\textsuperscript{7,8}.

As with any measurement technique, it is possible that derivative measurements,
if used incorrectly, may actually introduce errors larger than would have been observed
without its use. A basic understanding of the derivative concept will minimize this
possibility.

Hence it is appropriate to present the basic characteristics of derivative
spectrophotometry and to review the general analytical applications of DS introduced during
the last sixteen years (since 1994).

**Basic characteristics of derivative spectrophotometry**

**Increase of spectral resolution:**

The main characteristic of DS, the enhancement of the resolution of
overlapping spectral bands, is the consequence of differentiation which discriminates against
broad bands in favour of a sharp peak to an extent which increases parallel to the derivative
order\textsuperscript{5}. This property depends on the intrinsic band-width. For two representative simple
band shapes, Gaussian and Lorentzian, which are typical of the type encountered in practical
spectroscopy, the amplitude in the $n^{th}$ derivative order ($nD$) is inversely related to the $n^{th}$
power of the band-width ($W$) of the original spectrum:

\[
\frac{1}{W^n}
\]

\text{(5)}

Thus, if two bands (X and Y) are of the same intensity, but of different width,
the derivative amplitude of the sharper band (X) is greater than that of the broader one (Y) by
a factor that increases with increasing derivative order:
The relative increase of the amplitude of the sharper band compared to that of the broader one in higher derivatives, represents the most important factor responsible for the increase of sensitivity and selectivity in (DS) (fig.1.1). Unfortunately, instrument noise, which increases with derivative order, represents a limiting practical factor.

\[
\frac{\frac{n}{D(X)}}{\frac{n}{D(Y)}} \left( \frac{W_y}{W_x} \right)^n
\]

(6)

Fig. 1.1
Effect of derivative order (zeroth, second and fourth) on the relative amplitudes of two coincident Gaussian bands, X and Y, of equal intensity but with a bandwidth ratio 1:3
Fig. 1.3  
Reduction in the effect of a curved baseline by the derivative technique. (A) Chromophore absorption alone; (B) observed absorption of chromophore superimposed on baseline; (---) baseline alone
Elimination of the influence of baseline shift and matrix interferences:

Qualitative and quantitative investigations of broad spectra are frequently difficult, especially where the measurement of small absorbances is concerned, because of uncontrollable baseline shift, great blank absorption of light scattering by turbid solutions and suspensions. All these influences can be overcome by derivatisation (figs. 1.2 and 1.3). The order of derivatisation depends on the order of the polynomial function used to describe interferences. In general, if 'n' represents the highest degree of the polynomial equation used to define an interference, then the interference is reduced to a constant by using the n\textsuperscript{th} order derivative and is completely eliminated in the (n+1)\textsuperscript{th} derivative:

\[ P = a_0 + a_1 \lambda^1 + a_2 \lambda^2 + \ldots + a_n \lambda^n \] \hspace{1cm} \text{(7)}

\[ \frac{d^n P}{d\lambda^n} = n! a_n \] \hspace{1cm} \text{(8)}

\[ \frac{d^{(m+1)} P}{d\lambda^{(m+1)}} = 0 \] \hspace{1cm} \text{(9)}

In many cases, matrix interference can be described by a linear function (\( P = a\lambda + b \)), the first derivative yields a function where the interference is reduced to a constant (\( \frac{dp}{d\lambda} = a \)) and in the second order derivative transformation the interference is completely eliminated (\( \frac{d^2 p}{d\lambda^2} = 0 \)).

Enhancement of the detectability of minor spectral features:

Derivatisation of broad spectra increases both the possibility of detection and measurement of minor spectral features and discrimination against interference. Also, it should be kept in mind that derivative transformation of broad spectra does not increase the number of intrinsic data (as a matter of fact, some could be lost as a constant factor) but...
visually enhances subtle changes in them. Besides qualitative information, this provides wide possibilities for quantitative analysis in cases when the main peak is obscured by an intensive interfering peak (fig.1.3) and for analysis of multi component mixtures. Although, a great number of theoretical and practical investigations have been developed so far, a general approach to the application of DS in quantitative analysis is impossible, because each combination of bands and the degree of their overlapping tends to be an individual case.

**Precise determination of the positions of absorption maxima:**

When a single-peak spectrum has a broad band as its main feature, the position of the absorption maximum can be only approximately determined. The first derivative of this band (dA/d\(\lambda\)) passes through zero at the peak maximum, minimum and shoulder points (fig.1.4) and can be used to accurately locate the peak position. In contrast, the second and higher even derivatives (\(d^2A/d\lambda^2\), \(d^4A/d\lambda^4\),......) contain a peak of changeable (fig.1.4) sign (negative in the second order, positive in the fourth order, etc.) which has the same position as a peak maximum in the normal spectrum. The width of this peak progressively decreases with increasing order of the even derivative, which causes a sharpening of the peak enabling its exact identification. However, every even derivative peak is accompanied by symmetrical satellites of the opposite sign, the number of which is equal to the derivative order. In higher order derivatives (\(n>6\)) the satellites of adjacent bands may interfere, thus limiting the observed resolution. Also, during differentiation of spectral profiles, peaks of certain components might be shifted, compared to their original positions.

**Signal-to-noise ratio (SNR):**

The main disadvantage of the derivative technique is that the SNR becomes worse as the order of the derivative increases. A detailed study on the effect of derivatisation on the SNR, together with a general approach for the optimization of the SNR on examples of Gaussian and Lorentzian bands has been described by O.Haver. The noise of the zeroth-order derivative may be expressed as the standard deviation of all the elements in a series consisting only of noise, i.e., when there is no signal.
Zero order

Characteristic profiles of derivative orders of a Gaussian band

Fig. 1.4  Characteristic profiles of derivative orders of a Gaussian band
The standard derivation of the \( n \) order derivative can be calculated by usual the rules for error propagation. The relative SNR of the \( n^{th} \) derivative without smoothing is given by the following expression:

\[
\frac{(\text{SNR})_n}{(\text{SNR})_0} = \frac{C_n}{M^n} \quad \text{(10)}
\]

where \( C_n \) is a constant which depends on the derivative order and the type of the band; \( (\text{SNR})_0 \) represents the SNR of the unsmoothed zeroth derivative; \( M \) is the number of points in the peak full-width at half maximum (FWHM). For example, if \( M=10 \) the relative SNR of the first four derivatives are 0.20, 0.032, 0.008 and 0.0017 in Gaussian bands and 0.018, 0.041, 0.017 and 0.0064 in Lorentzian bands. Clearly, if \( M \) is large, the SNR of higher derivatives will be very poor even if the SNR of the original spectrum is satisfactory. Therefore, the practical derivative technique includes a certain degree of low-pass filtering or smoothing to control the noise increase which is an inevitable consequence of a noise signal differentiation. The effect of smoothing a peak-type signal is to reduce the noise, which is desirable and to distort the signal, which is undesirable but unavoidable. The distortion is seen as attenuation in the peak height and a slight increase in the width. The extent of this distortion depends on the smoothing ratio (the ratio of width of the smooth to the FWHM) and the number of times that the smoothing is passed through the data series (the sliding average and quadratic-cubic types of smoothing function require \( n+1 \) passes for the \( n^{th} \) derivative). The trade-off between peak height attenuation and the relative SNR as a function of smoothing ratio is illustrated in fig (1.5) for the second derivative of a Gaussian band.

The selection of the optimum smoothing ratio depends on the purpose for the application of derivative technique. When used for the purpose of resolution enhancement, a relatively small smoothing ratio will assure that a small loss in effective resolution will result. In such a case a significant loss in the SNR will have to be tolerated. In quantitative applications, when the derivative technique is used to remove or reduce band background, significantly larger smoothing ratios may be profitably employed.
Fig. 1.5  Attention factor (1) and relative signal to noise ratio (2) as a function of the smoothing ratio for the second derivative of a Gaussian band.
Since the origin of noise can be different, depending on both the instrument and the sample, the smoothing process involves optimization of all available instrumental parameters (full-scale response, slit width, scan speed, absorbance units) to be used for a particular problem on a particular instrument\textsuperscript{10-14}.

**Quantitative analysis:**

The application of DS for quantitative analyses is based on the same requirements as normal spectrophotometry, i.e., the validity of Beer's law and the additivity of absorbances\textsuperscript{15}. For the derivative spectra of the \( n \th \) order at a wavelength \( \lambda \), these laws can be represented by the following equations.

\[
\frac{d^n A}{d\lambda^n} = \frac{d^n \varepsilon}{d\lambda^n} \quad \text{cb} \quad \text{............... (11)}
\]

\[
\frac{d^n D}{d\lambda^n} = \frac{d^n D(T)}{d\lambda^n} = \frac{d^n D(X)}{d\lambda^n} + \frac{d^n D(Y)}{d\lambda^n} + \text{.....} \quad \text{............... (12)}
\]

Where \( A \) is the absorbance, \( \varepsilon \) represents the molar absorptivity, \( c \) is the concentration, \( b \) is the path length and \( nD(T) \) is the total derivative amplitude, which is equal to the algebraic sum of each absorbing component \( X, Y, \) etc. The application of these laws is based on a previous choice of optimal conditions, which include the selection of the most appropriate analytical bands, the suitable derivative order, and the method of measurement and optimization of all significant instrumental parameters. The most important methods used for the construction of a calibration curve are: peak-peak, peak-baseline, peak-tangent and zero-crossing (fig.1.6 and 1.7)\textsuperscript{15-19}. Sometimes, numerical methods of measurement, such as derivatisation of the "ratio spectra", are used\textsuperscript{20}. The measurement method of choice, in practice, would to be the one showing the best linear dependence on the concentration of the analyte, a zero or near zero intercept at the origin and be the least influenced by the concentration of any other component.
Fig. 1.6  Graphical measures for amplitudes in derivative Spectrophotometry:
(p) peak-peak method;
(t) peak-tangent method;
(z) peak-baseline method.
Fig. 1.7  *Use of the zero-crossing technique to allow quantitation of one chromophore (X) overlapped by the absorption band of another chromophore (Y).*
The usage of more than one derivative order in a particular case, as well as the measurement of the amplitude at several wavelengths, caused the need for the introduction of a notation rule for the amplitude values. Fasanmade and Fell\textsuperscript{10} proposed a generally applicable method. The letter D is used to indicate that the amplitude of the peak has been measured in the derivative domain. The order of derivative is specified by a leading superscript to the letter D. e.g., D\textsuperscript{1}, D\textsuperscript{2}, D\textsuperscript{3}. The two wavelengths between which the derivative peak is measured are specified by subscripts separated by a comma. The first wavelength corresponds to the more positive amplitude value while the second one defines position of the more positive amplitude value while the second one defines position of the more negative value. The peak is measured with respect to the zero baselines at the same wavelength and only one wavelength needs to be specified.

**Analytical applications:**

**(1) Inorganic analysis**

Due to its increased selectively and sensitivity compared to classic spectrophotometry, DS is widely applied in inorganic chemistry for the simultaneous determination of trace elements of similar chemical properties present in mixtures at different concentration levels. For the purpose, the first and the second order derivative are usually used, although in some cases higher-order derivatives provide more reliable results\textsuperscript{21,22}.

Simultaneous determination of rhodium and iridium is reported using derivative spectrophotometry after pre concentration of their 2-(5-Bromo-2-pyridyazo)-5-diethyminophenol\textsuperscript{23} (5-Br-PADAP) and tetraphenylborate onto microcrystalline naphthalene in the pH ranges 5.0-6.5 and 3.5-5.5 respectively. The solid mass obtained after filtration is dissolved in 5ml of dimethylformamide (DMF). A derivative spectrophotometric method using a zero-crossing technique measurement is described for their simultaneous determination in mixtures. The determination of rhodium and iridium in the concentration ranges 0.15-12.5 and 0.25-10.0\textmu g/ml in 5ml of the final DMF solutions respectively.
Favorable selectivity in the presence of common ions is achieved by adding EDTA after complex formation various parameters are studied in order to optimize the conditions for the simultaneous determination of rhodium and iridium in various synthetic samples corresponding to their standard alloys.

Most of the DS methods aimed at the simultaneous determination of inorganic substances are developed till 90s, but scientific interest directed towards further developments and improvements of these approaches is still intensive, since DS frequently represents the method of choice for the determination of inorganic substances.

A first-order derivative method is described for the simultaneous determination of mixtures containing nickel, copper and zinc, and cobalt, nickel, zinc and iron using PAR as the chromogenic reagent. The same reagent is applied in a second-order derivative method for the determination of nickel (II) (0.20-1.25ppm) and cobalt (II) (0.25-1.25ppm) in a mixture. Mathew et al. developed a first-order derivative method for the simultaneous determination of copper (0.012-0.25 μ g/ml), mercury (0.025-0.25 μ g/ml) and lead (0.025-0.25 μ g/ml) using dithizone as the reagent. Based on the three-component colour system of 2-(5-bromo-2-pyridylazo)-5-(diethyl amino) phenol cetylpyridinium bromide, a DS method is developed for the analysis of manganese, copper and zinc in an aluminium alloy. The determination of aluminium content in some pharmaceuticals is achieved by derivatisation of the spectrum of the content in some pharmaceuticals is achieved by derivatisation of the spectrum of the complex of aluminium and oxine-5-sulphonic acid at pH 4.5. also, the estimation of nickel(II) (detection limit 0.2mg/ml) in the presence of cobalt is performed by applying first-order DS on the complex of nickel and 2-(5-bromo-2-pyridylazo) (5-diethylamino) phenol in the presence of triton X-100. in addition, application of DS served to develop methods for Cu(II) (detection limit 4.0 mg/ml) determination in non-ionic micellar medium with 1-(2-pyridylazo)-2-naphthol (PAN) in the presence of the neutral surfactant triton X-100. The method has been applied in the quality control of numerous commercially available alcohol beverages, biological samples and standard alloys. Taher et al. used the same reagent (PAN) to measure iridium after preconcentration of its complex on microcrystalline naphthalene and the application of first order DS diminishes the detection
limit to 20 ppb. Different parameters significant for the optimization of the experimental conditions have been studied in relation to the determination of iridium in synthetic samples corresponding to various standard alloys and environmental samples. Besides, a very sensitive and selective DS method for the measurement of palladium (II) in the form of its complex with a novel reagent pyridopyridazine dithion (PPD) has been developed. The detection limit determined by normal spectrophotometry is 0.2μg/ml (0.1 g/ml in the presence of triton X-100), while the significantly lower detection limit of 3.7 ng/ml is achieved using the fourth-order derivative mode. The method is free from interference by most common metal ions and anions and it is successfully applied to the determination of palladium present in activated charcoal. A first-order DS method for the simultaneous determination of Pd (II) and Co (II) with diethylenetriamine-pentaacetic acid (DTPA) has been developed by Perez-Iglesias et al.

Second-order DS is applied in the determination of neodymium, holmium and erbium in mixed rare earths by norfloxacin. The RSDs are 1.0, 1.4 and 1.1% for 6.9×10⁻⁵ mol/l Nd, 6.0×10⁻⁵ mol/l Ho and 6.0×10⁻⁵ mol/l Er, respectively. This procedure is also used to measure small amounts of dysprosium, holmium and erbium. First order DS is applied for the determination of nickel in alloys and biological samples after preconcentration with the ion pair of 2-nitroso-1-naphthol-4-sulphonic acid and tetradecylmethylbenzylammonium chloride onto microcrystalline naphthalene or by a column method. Detection limit is found to be 0.3 μg/ml. for the optimization of the experimental conditions in the determination of nickel in standard alloys and biological samples, different parameters have been examined. DS methods for the estimation of micro amounts of nickel and aluminium in alloys have been developed applying 2-(5-bromo-2-pyridylazo)-5-phenol as the reagent. The matrix Al and Co alloying elements Ti, Mn, Zn, Mg, Pb, Sn, V, Ga, Zr, rare earths, Cu, Fe, Co, are masked with fluoride, tartarate, Na₂S₂O₃, thiourea, pyrophosphate or nitrite. The RSD is <7% and the recovery 97-105%. A derivative double wavelength photometric method is developed for the simultaneous determination of cobalt and nickel in heavy oil. P-5-Br-PADAP is used as the colour developing system after the separation of the interfering elements. The RSD for the determination of Co and Ni are 2.8 and 7.8% and the recovery 94.0 and 100.0% respectively.
Simultaneous derivative spectrophotometric determination of cobalt (II) and nickel (II) is reported using dithizone\(^\text{40}\). 1-(2-thiazolylozo)-2-napthol\(^\text{41}\) is used for the second derivative spectrophotometric trace determination of scandium in biological samples. Rapid derivative spectrophotometric method for the determination of platinum\(^\text{42}\) in Pt-Ru/C-catalyst using iodide is reported. Fe\(^{2+}\) and Fe\(^{3+}\) are determined simultaneously by second derivative spectrophotometry be Keveser Sozgen et al\(^\text{43}\). A first derivative spectrophotometric method for the simultaneous determination of zirconium and molybdenum with Alizarin Red S is reported\(^\text{44}\). Fourth derivative spectrophotometry is employed for the trace determination of silver\(^\text{45}\) by Mohammad Ali Taher et al. Selective determination of platinum (IV) and palladium (II) in iodide media by derivative spectrophotometry\(^\text{46}\) is employed for their determination in silver alloy.

A procedure has been developed for the fourth-derivative spectrophotometric determination of iron (III) dimethyldithiocarbamate by converting it into (II)-2, 2-bipyridyl complex\(^\text{47}\), which is then dissolved in triton X-100. Beer's law is obeyed over the concentration range 0.5-20\(\mu\)g/ml. Various parameters such as the effect of pH and interference of large number of ions in the determination of ferbam have been studied in detail. The method is sensitive and can be used for the determination of ferbam in a commercial sample and in mixtures with various dithiocarbamates (ziram, zineb, maneb, etc.) and from wheat grains.

A novel and highly sensitive first derivative spectrophotometric method is proposed for the determination of vanadium (V) and iron (III) ions separately and simultaneously in a mixture. 2-Hydroxy-1-naphthaldehyde benzyolhydrazone\(^\text{48}\) (OHNAH) reacts with vanadium (V) and iron (III) ions separately and simultaneously in a mixture. 2-Hydroxy-1-naphthaldehyde benzyolhydrazone (OHNAH) reacts with vanadium (V) and iron (III) in sodium acetate-acetic acid buffer medium forming yellow and yellowish brown colored soluble complexes respectively. A very simple and accurate simultaneous first derivative method is also reported for the determination of V (V) and Fe (III) in mixtures. The method is applied for the analysis of various natural samples, food and biological materials.
The reaction of \( \alpha \)-benzilmonoxime with palladium (II) produces a green complex in triton X-100 micellar media. Palladium has been determined using zero and first derivative spectrophotometric methods. The absorbance of Pd (II)-\( \alpha \)-benzilmonoxime\(^{49}\) complex at 441.8 and 667 nm in 0.10 M and 0.7-20.0 \( \mu \)g/ml with detection limits of 0.07 and 0.10 \( \mu \)g/ml are obtained respectively. Also recoveries in the range of 92.8 to 100.1% and relative standard deviations in the range of 0.4 to 7.1% are obtained. First derivative spectroscopy has also been applied for palladium (II) determination under the optimum condition. The linear dynamic range of 0.2-24.0 \( \mu \)g/ml of palladium (II) with relative standard deviations of 0.6-6.9% and recoveries in the range of 94.9-102.5% has been obtained by first derivative spectrophotometry. The method shows high selectivity because of the high concentration of acid used, which prevents formation of complexes of \( \alpha \)-benzilmonoxime with the other cations. The method is successfully applied to the determination of palladium in some synthetic palladium alloys and palladium charcoal powder.

A new derivative spectrophotometric method for rapid and selective trace analysis of Ga(III) and In(III) and their simultaneous determination using 2-(5-bromo 2-pyridyazo)-5-diethylaminophenol\(^{50}\) in cationic micellar medium is reported. Molar absorptivity and Sandell's sensitivity of 1:1 Ga (III) and In (III) complexes at 553 nm and 558 nm are \( 7.22 \times 10^4 \) l mol\(^{-1} \) cm\(^{-1} \) and 5.85\( \times 10^4 \) l mol\(^{-1} \) cm\(^{-1} \) and 0.96 ng/cm\(^2 \) and 1.96 ng/cm\(^2 \), respectively. Linearity is observed in the concentration range 0.023-0.700 \( \mu \)g/ml for gallium and 0.076-1.520 \( \mu \)g/ml for Indium. These metal ions interfere with the determination of each other. However, 0.07-0.70\( \mu \)g/ml Ga (III) and 0.115-1.150\( \mu \)g/ml In (III) could be determined simultaneously when present together have been successfully applied for the individual and simultaneous determination of gallium and indium in synthetic binary mixtures, standard reference materials and environmental samples.

A simple, sensitive and rapid derivative spectrophotometric method using 2-(5-bromo-2-pyridylazo) 5-diethylaminophenol (5-Br-PADAP)\(^{51}\) has been developed for simultaneous determination of Co(II), Ni(II) and Fe(II) which have very similar chemical behaviors and appear together in many real samples. The complexes of all these metal ions with 5-Br-PADP are formed immediately at pH 7.0 ammonium acetate buffered solution and
are stable for at least 24 hours. Second derivative spectra are selected for evaluation, because working wavelength determination is more precise and spectral overlap is less than in the ordinary and first derivative spectra. Three wavelengths at which the complexes exhibit $^2D$ values for Co (II), Ni (II) and Fe (II) are selected as analytical wavelengths i.e., 640, 600 and 740 nm respectively. Calibration plots drawn with zero to peak values at above mentioned wavelengths are linear between 80 and 2000 ng/ml for each metal ion. Concentration of Co (II) and Ni (II) are calculated from the $^2D$ values and the sum of linear equations for these three cations at 640 nm, after Fe(II) assay by making use of $^2D$ value at 740 nm. Limits of detection (LOD) for Co (II), Ni (II) and Fe (II) are 2.7, 13.9 and mg/ml, respectively. The method has been applied to tool steel and heat resistant wire samples successfully.

Simultaneous derivative spectrophotometric determination of zinc and cadmium with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol in the presence of acetylpyridinium chloride is reported\textsuperscript{52}.

Simultaneous perconcentration of vanadium (V/IV) species with palmitoyl quinolin-8-ol bonded to amberlite XAD 2 and their separate spectrophotometric determination with 4-(2-pyridylazo)-resorciinol using CDTA as masking agent is reported by Hayati Filik et.al\textsuperscript{53}.

2) Organic and pharmaceutical analysis:

Methods for the determination of organic substances by the DS technique have been developed mainly for application in the analysis of pharmaceuticals and/or clinically and biochemically interesting systems. The interference of the formulation excipients or other UV-absorbing components, such as co-formulated drugs and degradation products, usual in conventional UV-spectrophotometry can be successfully eliminated by the DS technique.
A variety of producers that render the DS determination of drugs more specific and sensitive, regardless of whether they are determined as single compounds or in mixtures, have been published.

First and second order DS methods have been proposed for the assay of the anti inflammatory drugs fentiazac, flufenamic acid, tiaprofenic acid and proquazone. Similar methods have been developed for the determination of several other drugs alone, such as metronidazole (1.20µg/ml) in tablets\textsuperscript{55}, carboplatin (5-150µg/ml)\textsuperscript{56}, anthralin in ointments\textsuperscript{57} and paracetamol in blood sera\textsuperscript{58}.

Aspirin, phenacetin and caffeine in analgesic tablets have been determined by zero crossing derivative spectrophotometry\textsuperscript{59}. Chlorpheniramine maleate, codeine phosphate and ephedrine hydrochloride have been estimated without separation using second-order DS. Chlorpheniramine maleate (0.001-0.080 mg/ml) and codeine hydrochloride (0.005-1.80 mg/ml) is determined after oxidation with sodium periodate\textsuperscript{60}. For quality control of pharmaceutical preparations containing clozapine, two analytical procedures are developed: HPLC (5.150µg/ml) and DS (5.50µg/ml) suitable for different levels of the drug\textsuperscript{61}.

Numerous papers published so far relate to analyses of drugs in mixtures. Thus, methods for determination of paracetamol and phenoprobanate by first-order DS\textsuperscript{62}, mixtures of cocaine, procaine and lidocaine in pulver samples by second order DS\textsuperscript{63}, paracetamol (10.40µg/ml) and caffeine (1.3µg/ml) in tablets by first and second order DS\textsuperscript{64}, acetylsalicylic acid free salicylic acid in sustained release tablets\textsuperscript{65}, cetrimide and chlorhexidine glyconate in antiseptic solutions by first order DS\textsuperscript{66} have been described. Fourth order DS procedures have been used for the determination of clopramide and pindolol in tablets\textsuperscript{67}, lidocaine hydrochloride and 5-nitrox in liquid formulations\textsuperscript{68}. Also DS methods have been described for the assay of phenobarbitone in mixtures with oxyphenonium bromide and meprobamaate, paracetamol or acetylsalicylic acid (first and second order)\textsuperscript{69}, procaine hydrochloride with benzoic acid, pyridoxine hydrochloride, 4-aminobenzoic acid\textsuperscript{70}, (0.5-14.0µg/ml) sulfanilamide and (1.20µg/ml) sulfadiazine (third DS)\textsuperscript{71} and sulfamethoxazole and trimethoprim (second order DS)\textsuperscript{72}.
Derivative procedures reported for vitamin mixtures are concerned with pyridoxine hydrochloride and thiamine hydrochloride in tablets (first and third order)\textsuperscript{73}, vitamins B (0.2\mu g/ml), B (0.46\mu g/ml); and B (0.22\mu g/ml), uridine 5-triphosphate (0.2\mu g/ml) in injections (second order),\textsuperscript{74} and sodium salicylate, thiamine hydrochloride and ascorbic acid in visalicyl tablets (first and second order)\textsuperscript{75}. First derivative measurements have been used to determine benzimidazole and cinnamate, as well as benzophenone derivatives in order to characterize sun-screens in cosmetic formulations\textsuperscript{76}. First and second order DS have been described for evaluating bilirubin, albumin and oxyhemoglobin in amnionic fluid\textsuperscript{77}.

First order DS is used for the determination of intact ceftazidime (5.50\mu g/ml) cefuroxime sodium (5.35\mu g/ml) and cefotaxime sodium (5.40\mu g/ml) in the presence of their degradation products\textsuperscript{79}. Second and third order DS are used for the estimation of acyclovir in the presence of diloxanide (a degradation product)\textsuperscript{79}. The accuracy of the proposed method is found to be better than that of a classical approach.

For a simultaneous determination of acetaminophen and phenobarbital after their extraction from the corresponding suppositories with borate buffer, pH 10, a first order DS method is developed\textsuperscript{80}. In addition, a new spectrophotometric method is described for the simultaneous analysis of a ternary mixture containing etamizole, paracetamol and caffeine\textsuperscript{881}. This method is based on the use of the ratio spectrum derivative obtained by dividing the absorption spectrum of the ternary mixture by a standard spectrum of a mixture containing two of the there compounds in the title mixture. This method applied for the assay of tablets is compared with the alternative spectrophotometric method. First (zero-crossing) and fourth order (amplitude-baseline) DS methods for determination of triamterene and hydrochlorothiazide, respectively, in combined tablets have also been described\textsuperscript{82}. A first order DS method has been developed for the simultaneous determination of rifamycin SV sodium and lidocaine hydrochloride in injection solutions\textsuperscript{83}. The simultaneous determination of ethinyl estradiol and norgestrel in tablets utilizing first order DS has been reported\textsuperscript{84}, as well.
Three accurate and simple methods (first order DS, simultaneous equation and multi component mode) for the simultaneous determination of tinidazole and furazolidone in tablet formulations have been developed\(^8\).

A method for the simultaneous determination of melatonin pyridoxine combination in tablets by the zero-crossing technique of the first and second order DS has been reported (RSD<2\%). This method is successfully applied for the determination of both drugs present in laboratory prepared mixtures and in tablets\(^8\). For the evaluation of diclofenac and benzyl alcohol as an excipient in injectable formulations, the first and second order DS method using the zero crossing technique has been described\(^8\). In addition, three new methods (first order DS, ratio spectra DS and Vierodt’s method) for the quantitative analysis of tablet formulations containing pseudoephedrine hydrochloride and tripolidine hydrochloride are developed developed and compared\(^8\). A rapid, simple and direct assay procedure based on first order DS using zero crossing and peak-to-base measurements for the determination of dextromethorphan HBr (detection limit 0.033\(\mu\)g/ml) and bromhexine HCL (detection limit 0.103\(\mu\)g/ml) has also been developed\(^8\). Further, a simple and economical DS procedure is described for the simultaneous determination of indomethacin and paracetamol in combined dosage forms\(^9\). Applying the zero-crossing technique of the second order DS a method for the determination of 1,4-benzodiazepin, midazolam\(^9\) and lorazepam\(^9\) in tablets is developed. Midazolam is estimated in the presence of maleic acid as a co-formulation, while lorazepam is measured in the presence of degradation products.

Finally, the simultaneous derivative spectrophotometric technique is applied for the determination of various organic compounds, such as the pesticides atrazine (1.15\(\mu\)g/ml), diuron (1.10\(\mu\)g/ml) and chlorpyrofos (1.10\(\mu\)g/ml) in ground waters and soil, sodium p-nitrophenolate, and 2-methoxy-5-nitrophenolate in plant and animal growth regulators\(^9\), tyrosine, tryptophan and phenylalanine\(^9\) and phenol and cresol in the presence of pyrocatechol and resorcinol. Using the first and second order derivatives of the spectra ratio, a method for the analysis of binary mixtures of the flavonoids chrisin and quercetin has been described\(^9\). A third derivative method using the zero-crossing technique has been employed for the simultaneous determination of [dimethylamino]-ethyl (o-chloro-(dimethylamino) sulfonylephoxyl acetate hydrochloride and its major hydrolytic
decomposition product o-chloro-p-(dimethylamino) sulfonyl phenoxy acetic acid. A multi-wavelength linear regression derivative spectrophotometric method for the determination of phenol, hydroquinone and catechol has also been described.

Synthesis of meso meso-tetra-(3,5-dibromo-4-hydroxyphenyl)-porphyrin and its application to second-derivative spectrophotometric determination of lead in clinical samples is reported.

Simultaneous determination of atropine sulfate and morphine hydrochloride in their binary mixture using spectrophotometric methods is proposed by Dinç, Erdal; Onur, Feyyaz. In this study, four spectrophotometric methods are used for simultaneous determination of atropine sulphate and morphine hydrochloride in their binary mixture. In the first and second methods Vierordt's and modified Vierordt's methods, quantitation of atropine sulfate and morphine hydrochloride are realized by using A (1%,1 cm) values determined at 257.3 nm and 284.4 nm in their solution in distilled water. In the third method, derivative spectrophotometry, dA/dλ values are read at 260.8 nm for atropine sulfate and of 244.7 nm for morphine hydrochloride in the first derivative spectra of both compounds. In their solution, in distilled water. In the fourth method, ratio spectra derivative spectrophotometry, analytical signals are measured at 255.8 nm for atropine sulfate and 273.6 nm for morphine hydrochloride in the first derivative of ratio spectra obtained by using their spectra as divisor in their solution in distilled water. The procedures do not require any separation step. Mean recoveries and relative standard deviations of the methods are calculated in synthetic mixtures.

Furfural and 5-(hydroxymethyl)-2-furaldehyde (HMF) are useful indicators of accurate storage temperature of food samples. A first derivative spectrophotometric method is developed for the determination of the furfural and HMF level in locust bean pekmez. In addition, the levels of the furfural and HMF are investigated during locust bean pekmez preparation; the recoveries are generally nearly 100%. This method is also rapid and accurate and results in economical analyses of furfuraldehydes.
A method for the determination of cetirizine dihydrochloride\textsuperscript{104} in pharmaceuticals by first, second, third and fourth derivation spectrophotometry is described using "Peak-Peak" (P-P), and measurements. The calibration curves are linear within the concentration range of 7.5-22.5 $\mu$g/ml for cetirizine dihydrochloride. The procedure is simple, rapid and the results are reliable.

Derivative spectrophotometry is applied for the simultaneous determination of amoxicillin and clavulanic acid\textsuperscript{105} in pharmaceutical preparations, "Augmentin" injection and tablets and "Amoksiklav" drops and tablets, in solution after hydrolysis with sodium hydroxide. As the absorption spectra overlap strongly (Amoxicillin) $\lambda_{\text{max}} = 247$ nm and 290nm, clavulanic acid $\lambda_{\text{max}} = 258$ nm, the first and the second derivative spectrophotometric procedure is described for their determinations. Amoxicillin is determined at $\lambda = 257.9$ nm (first derivative spectra) or $\lambda = 273$ nm (second derivative) while clavulanic acid at $\lambda = 280.3$ nm (first derivative) or $\lambda = 285$nm (second derivative spectra). Beer's law is obeyed in the range of 0.004-0.04$\mu$g/ml for amoxicillin and 0.002-0.02 mg/ml for clavulanic acid. A simple and rapid derivative spectrophotometric assay procedure is described for the analysis of castine (1), acetaminophen (2) and propyphenazone (3) in tablet formulations. The concentration range of application is 50-250 $\mu$g/cm$^3$ for 2 and 3 and 10-50 $\mu$g/cm$^3$ for 1. The method involves the extraction of the drugs from tablets with 0.1 N H$\text{SO}_4$, filtration, appropriate dilution, and measurement of the fourth derivative absorbance values at zero crossing wavelengths of 230.0, 263.6 nm for 1,2 and 3. As a reference method, a reversed phase HPLC procedure is developed. Commercially available tablets re analyzed. Statistical comparison of the results with those obtained from reference method showed good agreement. The derivative spectrophotometric method has the advantage of being simple, rapid, inexpensive, and easy to perform.

Caffeine\textsuperscript{107} content is determined in cola, coffee and tea by second and third order derivative spectrophotometry without using any separation or background correction technique and reagent. The method is based on the measurement of the distances between two extreme values (peak to peak amplitudes) in the second order (cola) and third order (coffee and tea) derivative spectra of the sample solution. Calibration curves are constructed for the 2.0-10.0$\mu$g/ml concentration range. As a reference method, reversed phase high
A first derivative spectrophotometric method is developed\textsuperscript{108} for the determination of parathion and p-nitro phenol in vegetable tissues. Ethanol is used as solvent for extracting the compounds from tissues and subsequently the samples are evaluated against a vegetable tissue blank, directly by derivative spectrophotometry. The simultaneous determination of these compounds can be carried out using the zero-crossing approach for parathion at 253.0 nm and for p-nitro phenol at 273.1 nm. In the samples each analyte is determined in the presence of one another in the ranges between 4.9 to 3883.5 µg/ml for p-nitro phenol. The detection limits are found to be 1.5 and 1.4 µg/ml for parathion and p-nitro phenol, respectively. The relative standard deviations are in all instances less than 1.8%. The proposed method is applied to the determination of the analytes in spiked leafs of corn.

Second derivative spectrophotometric determination of trimethiprime (TMP) and sulfamethoxazole (SM) in the presence of hydroxypropyl-β-CD has been reported\textsuperscript{109}. The calibration graphs are linear in the concentration range of TMP (1.92-19.2 µg/ml) and SM (1.60-16.50 µg/ml) the correlation coefficient for the calibration graphs is better than 0.9994 and the precision is satisfactory (CV%<4.96) in HP-β-CD solutions. The results are compared to those obtained by second derivative ultraviolet spectrophotometry in the absence of HP-β-CD thereby; the details of the statistical treatment of the analytical data are presented. A fast and accurate method for the determination of droperidol in the presence of methylparaben and propylparaben is developed using derivative spectrophotometry\textsuperscript{110}. The first derivative amplitudes at 255.2 nm are selected for the assay. Calibration graph follows Beer's law in the range of 5-35µg/ml. The co-efficient of variation (CV) for intra-day and inter-day precision are less than 1.0 and 2.0% respectively. The method is applied in the quality control of commercial oral and injection solutions and proved to be suitable for routine analysis. Derivative spectrophotometric method for the determination of phenyl-β-naphthlamine (PBN) used as an antioxidant in rubber mixtures has been described\textsuperscript{111}. The derivative spectrophotometric method indicated that the amount of PBN found after extraction from the rubber samples is 0.97±0.02g/100g of samples.
Simple, fast and reliable derivative spectrophotometric methods are developed for determination of indapamide in bulk and pharmaceutical dosage forms. The quantitative determination of drug is carried out using the first derivative values measured at 252.8 nm (N=6) and the second derivative values measured at 260.4 nm (N=9). Calibration graphs constructed as their wavelengths of determination are linear in the concentration range of indapamide using peak to zero 1.00-30.00μg/ml for first derivative and 1.00-35.00μg/ml for second derivative spectrophotometric method. New second derivative spectrophotometric methods for the determination of paramethrin in shampoo have been reported. The linear concentration ranges are 0.25-1.5 ppm (D =0.00042 conc.+0.0018,r=0.9972,n=10). Between day of CV%2.81, within day of CV% 3.50, and an analytical recovery close to 95-100% shows the suitability of the method for determination in quality control laboratories.

The simultaneous determination of domperidone maleate (DOM) and cinnarizine (CINN) in a binary mixture form is proposed, without previous separation, by two different techniques. The first method is the application of derivative spectrophotometry where the linearity range and percentage recoveries for DOM and CINN are 25-30 μg/ml, 5-25 μg/ml and 10006±1157, 9993±1377, respectively. The second method depends on the application of partial least squares (PLS) and principle component regression (PCR) models. A training set consisting of 10 mixtures containing 5-20μg/ml for each component is used for the construction of the PCR and PLS models. These models area used after their validation for the prediction are successfully applied for the simultaneous determination of both drugs in laboratory prepared mixtures and in commercial tablet preparations. The validity of the proposed methods is assessed by applying the standard addition technique where the percentage recovery of the added standard is found to be 9998±0297 and 9984±0700 for DOM and CINN respectively, using the derivative spectrophotometric method and 10029±0.398 and 10011±0.363 for DOM and CINN, respectively, using the PLS and PCR methods. The proposed procedures are rapid, simple, require no preliminary separation steps and can be used for routine analysis of both drugs in quality control laboratories. A derivative spectrophotometric method is developed for the three binary mixtures of psuedophedrine with fexofenadine (mix. I), cetirizine (mix.II) and loratadine (mix.III). The method is based on the use of the first derivative of the ratio spectrum. The concentration of the other component

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is determined from its respective calibration graph created similarly. Moreover, the influence of $\Delta \lambda$ for obtaining the first derivative of the ratio spectra and the effect of the divisor concentration on the calibration graphs are studied. The described method is applied for the determination of these combinations in synthetic mixtures and dosage forms. The results obtained are accurate and precise. A second order derivative UV spectrophotometric method for determination of vitamin C\footnote{ascorbic acid (AA)} content in a variety of natural samples is described. The method is based on the measurement of a peak-base line amplitude in the second derivative of the AA spectrum at 267.5 nm. The following corresponding regression equation is obtained with in the concentration range $2 \times 10^{-5}$ to $1 \times 10^{-4}$ M (35-176 mg/cm A>A) in 10M HCL solution. $D_{267.5} = 2420 \times 10^4 \times C + 0.025$; the correlation coefficient is 0.9993 and the detection limit $42 \times 10^{-6}$ M. The results obtained by analyzing 21 different species of fruits, vegetables and juices indicated a possibility for a more analyzed material, which makes it suitable for routine analyses. The reliability of the method is confirmed by comparative determinations with the generally accepted 2, 6-dichloroindophenol method.

A second order derivative spectrophotometric method for the determination of bifonazole in the presence of methyl-and propyl-p-hydroxybenzoate as preservatives has been developed\footnote{M. R. M. Geraditi, L. A. S. Prata, A. L. A. Riesco, A. C. S. R. J. J. A. 2012}. The determination is performed in a 0.1M HCL solution at 241.5 nm, a wavelength corresponding to the intersection of the second order derivative spectra (D) of methyl and dipropyl p-hydroxybenzoate with the axis (zero-crossing point). A calibration curve constructed for bifonazole concentrations ranging from 1.5 to 15 $\mu$g/ml had a correlation coefficient of 0.9998. Reliability and reproducibility of the method is checked by analyzing laboratory mixtures of bifonazole and preservatives (recovery 99.97-102.7%; RDS 0.48-1.46%). The proposed method is applied for the determination of bifonazole in a commercial cream formulation. The mean value of bifinazole obtained per 100 g cream is 1.029 of (102.9% of the labeled claim) with a RSD of 0.68%.

Development and validation of an analytical UV derivative spectrophotometric method to quantify losartan potassium\footnote{P. M. M. A. R. A. A. A. 2013} used as a single active principle in pharmaceutical forms are done. Based on the spectrophotometric characteristics of losartan potassium, a signal at 234 nm of the first derivative spectrum ($D_{234}$) is found adequate for quantification.
The linearity between signal D\textsubscript{234} and concentration of losartan potassium in the range of 4.00-6.00 mg/l in aqueous solution presents a square correlation coefficient ($r^2$) of 0.9938. The mean recovery percentage is 100.7±1.1% and precision expressed as relative standard deviation (RSD) is 0.88%.

A procedure has been developed for the direct fourth derivative\textsuperscript{119} spectrophotometric determination of tetramethyldithiocarbamate by converting it into copper (II) complex. Beer's law obeyed up to the concentration range 30 µg/ml. various parameters such as effect of pH, interference a large number of ions on the determination of thiram have been studied in detail. The method is sensitive, highly selective and can be used for the determination of thiram in commercial samples and from wheat grains.

Abstract chlorophyll a (Chl.a) and chlorophyll b (Chl. b) plant pigments, which are important in the food industry and are beneficial as environmental pollution indicators, have been extracted with a novel solvent mixture (1:1 v/v acetone-propanol) not containing chloroform and simultaneously determined by first derivative spectrophotometry has been reported\textsuperscript{120}.

A procedure has been developed for the fourth derivative spectrophotometric determination of tetramethyldithiocarbamate\textsuperscript{121} by converting it into its molybdenum complex, which is then extracted with methyl iso-butyl ketone (MIBK). Beer's law is obeyed over the concentration range 24µg/ml. the analytical sensitivity is calculated to be 0.004 (dA\textsuperscript{4}/dλ\textsuperscript{4}) µg/ml from the slope of the calibration curve. The detection limit is 0.3 µg/ml for thiram. Various parameters such as effect of acid concentration, interference of a large number of ions in the determination of thiram have been studied in detail. The method is sensitive, highly selective and can be used for the determination of thiram in a commercial sample, in mixtures with various dithiocarbamates (zineb, maneb etc.) and forms wheat grains.
3) Analysis of food and water:

Various derivative methods have been developed for the analysis of food. A simple extraction first order DS method for the determination of tartrazine (up to 3.0 μg/ml) and sunset yellow (up to 3.6 μg/ml) in commercially available products has been described. First order DS is applied also for the determination of tartazine in the presence of amaranth or carmoisine in different sugar candy samples. A very simple method for resolving ternary mixtures of food colorants, such as tartrazine, Sunset Yellow and ponceau 4R, by using the first derivative of the ratio spectra with measurements at the zero-crossing wavelength has been described. This method is applied for the analyses of synthetic mixtures of these colorants in different ratios with recoveries in the 94-105% range. Several other derivative methods have dealt with the simultaneous determination of colorants and dyes in mixtures such as carminic acid, riboflavin and erytrrosine in yoghurt samples and tetrazine, riboflavin, curcumin and eritrisine.

For detection of aromatic hydrocarbons in water samples, derivatives of the transmission spectrum with respect to wavelength are used. The method has as enhanced signal-to-noise ratio due to the generation of the derivatives in an optical manner. As examples of the application, monitoring of water samples for the presence of aromatic hydrocarbons, e.g., benzene, toluene and xylene, as well as process control in the chemical industry, are described.

Section-2 Hydrazones as spectrophotometric reagents - a brief review:

The compounds having the triatomic group >C=N-N< are generally called as hydrazones. These are distinguished from other members of this class such as imines, oximes etc, by the presence of the two interlinked nitrogen atoms. The hydrazone group occurs in the organic compounds of the following type.
Compounds having structure (I) are generally called as hydrazones, where as type (II) are named as azines.

Hydrazones are usually named after the carbonyl compounds from which they are derived. Many hydrazones are physiologically active and find applications in the treatment of diseases like tuberculosis, leprosy and mental disorder. Aryl hydrazones and isonicotinoyl hydrozones are potential agents for treatment of iron overload cancer and are also known for their antiproliferative effect. Di-2-Pyridyl ketone isonicotinoyl hydrazone and its analogues are capable of binding iron as tridentate (N,N,O) ligands. These compounds are highly cytotoxic but show selective activity against cancer cells. The interesting fact is that their cytotoxicity is maintained even after complexation with iron. They are also used as plasticizers and stabilizers for polymers and as polymerization initiators, antioxidants etc. Hydrazones act as herbicides, insecticides, rodenticides, plants growth regulators and also as intermediates in preparative chemistry. Hydrazones of 2-methyl pthalalzone are effective sterilizers for houseflies. 3-N-methyl-N-(4-chloro-1-phthalazinyl) and 3-N-methyl-N-(4-oxo-1-phthalazinyl) hydrazones posses anthelminitic activity. The complexes of some hydrazones are used in industry as dyes for wool, rubber and as photographic materials.
Preparation:

The sensitivity of reagents increases with increasing conjugation. One way of achieving conjugation is the use of an azo group to link two aromatic systems. This has two fold advantages as the azo group can also act as complexation site. Hydrazones are generally prepared by refluxing the stoichiometric amounts of the appropriate hydrazone and a carbonyl compound of high purity dissolved in suitable solvents. On cooling the compound usually crystallizes out. Detailed account of their preparation is given in a review. Many hydrazones are now commercially available.

Analytical applications:

Jain and Singh reviewed critically the application of hydrazones as analytical reagents. The formation of hydrazones is extensively used in the detection, determination and isolation of compounds containing the carbonyl group. Photometric methods for determining aldehydes and ketones are based on their reaction with 2,4-dinitriphenylhydrazine to from corresponding hydrazones. Bis cyclohexanone oxalylidihydrazone was one of the earliest used hydrazones for the spectrophotometric determination of copper. It gives a blue colour with traces of copper and was used for the determination of copper in pulp products, human serum, steel, plants, non-ferrous metals and alloys and in cadmium sulphide. Some of the hydrazones employed as spectrophotometric reagents for the determination of metal ions in recent times are listed in table 1.1.
<table>
<thead>
<tr>
<th>Reagent</th>
<th>Metal ion determined</th>
<th>Ref</th>
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<tbody>
<tr>
<td>p-Dimethylamino benzaldehyde</td>
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<td>isonicotinoylhydrazone</td>
<td>Hg(II)</td>
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<td>2-Hydroxy benzaldehyde isonocotinoyl hydrazone</td>
<td>Al(III), Zn (II),</td>
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<td></td>
<td>Co(II), Ni(II),Mn(II)</td>
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</tr>
<tr>
<td>Pyridine-2-aldehyde-2-pyridylhydrazone(PAPH)</td>
<td>Cu(II), Zn(II),</td>
<td>152, 153</td>
</tr>
<tr>
<td></td>
<td>Cd(II), Fe(II), Ni(II),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn(II),Pd(II)</td>
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<td>Picinaldehyde-2-pyridylhydrazone</td>
<td>Pd(II), Co(II)</td>
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<tr>
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<td>Cd(II)</td>
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<td>Naphthyl methyl ketone isonicotinoylhydrazone</td>
<td>Ti(IV)</td>
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<td>4-Hydroxy benzaldehyde isonocotinoylhydrazone</td>
<td>V(V)</td>
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<tr>
<td>2-Hydroxy-1-naphthaldehyde Isonicotinhydrazone</td>
<td>Mo(VI)</td>
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<td>Pyridine-2-aldehyde-2-quinolyhydrazone (PAQH)</td>
<td>Co(II), Ni(II), Cu(II)</td>
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<td></td>
<td>Fe(II), Pd(II)</td>
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<td>2,2'-Pyridyl bishydrazone</td>
<td>Fe(II),Cu(II),Co(II),Ni(II)</td>
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<tr>
<td>Phenyl pyruvic acid quinoylhydrazone</td>
<td>Cu(II)</td>
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<td>Thiophene-2-aldehyde-2-benzothiazoylhyclazone</td>
<td>Cu(II)</td>
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<td>Anthranilic acid isopropylidine hydrazone</td>
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<td>Salicylaldehyde isonicotinoylhydrazone</td>
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<td>Salicylaldehyde benzoylhydrazon</td>
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<tr>
<td>5-Methyl furfural-2-bensothiazoylhyclazone</td>
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<td>Furfural-2-benzo-thioazoylhyclazone</td>
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<td>5-Chloro-2-hydroxy acetophenone</td>
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<td>isonicotinoylhydrazone</td>
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<tr>
<td>Compound</td>
<td>Metal</td>
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<td>6-Methyl picolinaldehyde quinoylhydrazone</td>
<td>Pd(II)</td>
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<td>5-Chloro-thiophene-2-aldehyde-2-</td>
<td>Co(II), Cu(II)</td>
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<tr>
<td>Benzothiazoylhydrazone</td>
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<tr>
<td>Diacetylmonoxime P-Nitro phenylhydrazone</td>
<td>Co(II)</td>
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<td>Bisacetylazine hydrazone</td>
<td>Cu(II)</td>
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<td>Diacetyl-bis-(2-plyridyl)hydrazone</td>
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<tr>
<td>2-Hydroxy-1-naphthaldehyde</td>
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<td>185-187</td>
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<td>Benzothiazole-2-aldehyde quinolylhydrazone</td>
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<td>Pyridoin phenylhydrazone</td>
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<td>Pyridoin-2-carboxyaldehyde-2-hydroxy bezoylhydrazone</td>
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<td>Monohydrazone quinolylhydrazone</td>
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<td>2,2'-Bipyridyl-2-pyrimidylhydrazone</td>
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<td>Salicylaldehyde hydrazone</td>
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<td>2,4-Dihydroxy acetophenonme</td>
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<td>Thiazole-2-carbaldehyde-2-quinolylhydrazone</td>
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<td>2-Hydroxy acetophenone benzoylhydrazone</td>
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<td>Salicylaldehyde benzoylhydrazone and</td>
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<td>(\alpha)-(Benzimidazoly)-(\alpha,\alpha')-(N-5-nitro-2-pyridylhydrazone)-tolkuene</td>
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<td>Ni(II)</td>
<td>344</td>
</tr>
<tr>
<td>Deaceetylmonoxime-p-hydroxybenzoylhydrazone</td>
<td>Sn(II)</td>
<td>345</td>
</tr>
</tbody>
</table>
The plethora of hydrazones listed in the above table establishes their versatility as spectrophotometric reagents for the determination of metal ions and their biological activity. Among them, benzoyl hydrazone and their metal chelates are known for their importance both analytically and biologically. One benzoylhydrazone, namely 2,4-dihydroxybenzaldehyde-p-hydroxybenzoylhydrazone (2,4-DHBPHBH) has been synthesized and used as a spectrophotometric reagent for the determination of metal ions, Mo(VI), Ti(IV), V(V), Cu(II), and Fe(III). The results obtained are given in the following chapters. Highly sensitive and selective simultaneous derivative spectrophotometric methods are also reported for the determination of some important metal ions in binary mixtures.

Section-3 Importance of present investigations:

The precise determination of metal ions at micro gram levels in the area of analytical chemistry has given added impetus to the analytical chemists to discover simple speedy and accurate methods of innumerable methods presented in the literature, selecting a suitable method becomes difficult. Therefore in spite of the availability new method and modern techniques for the determination of metal ions, the demand for newer methods of analysis is increasing in view of problems constantly faced by the analytical chemist.

Although strong claims are made to the specificity and sensitivity of atomic absorption and plasma atomic emission analysis atomic fluorescence emission, some of the interferences to which these methods are subject to use poorly understood and continue to cause problems, further, these techniques are not within the reach of many laboratories. Besides of high cost and difficult to operate.

Therefore, spectrophotometry, a widely used analytical technique is familiar because of the common availability of instrumentation, simple, speed, precision and accuracy resulting in extensive of literature being published.
The advent of anew generation of spectrophotometers equipped with diode array detectors and extensive use of micro processors in data acquisition and handling have brought about dynamic progress in the simultaneous analysis based on multi wavelength and derivative measurements. Spectrophotometric analysis of metal ions at microgram level involves synthesis of selective and highly sensitive reagent. Among the various organic photometric reagents used, hydrazones occupy a special place due to their good chelation with metal ions and form more stable as well as characterized complexes.

Of the hydrazone depravities, p-hydroxy benzoylhydrazone are potential analytical reagents due to the capacity of their molecules to form insoluble complexes spectra when reacted with transition metal ions. Presence of hydroxyl group, ring rationing group at rare position is an additional feature for the chelating property. Therefore, p-hydroxy benzoyl hydrazones serves as better separating reagents, even at sub microgram level.

Of innumerable spectrophotometric methods available for the determination of almost all the metal ions in the periodic table at microgram levels, these methods suffer either from lack of specificity or selectivity. Further it is also difficult to develop a highly selective spectrophotometric procedure for a given metal ion making use of a given organic reagent in view of matrix differences. This necessities the development of more or less complicated procedures to overcome with detrimental influence. Therefore, in order to achieve grater degree of selectivity, the emphasis is being denoted to develop derivative spectrophotometric procedures and derivative spectrophotometric procedures for the determination of metal ions in admixture area sparsely reported in the literature.

In addition, derivative spectrophotometry is an excellent background elimination technique which enables the exact determination of $A_{\text{max}}$ of the particular analyte species and facilitates the detection of poorly resolved absorption peaks and also increases the sensitivity and enhances the selectivity of the spectrophotometric procedures. Further, this enables the simultaneous determination of two species with or without the need to solve simultaneous equations. But only few data have been reported on the determination of mixture of metal ion.
Section-4 Objectives:

An analytical method plays a vital role to product the composition of raw materials and finished products in controlling various processes in metallurgy and in the analysis of environmental pollutants. The analytical chemistry of some transition metals like cobalt and nickel high purity are widely employed in electronics industries and as catalysis.

p-Hydroxy benzoic hydrazones play a vital role as analytical reagents. The sensitivity of a reagent is enhancing with the increase in conjugation and presence of a phenolic group. Ring activating group at Para position. Further, the presence of a phenolic group or this to the chromophoric group enhances the sensitivity of the spectrophotometric determination.

Detailed study of the past work c.f. section 1) reveals that very few p-hydroxybenzoic hydrazones are employed as analytical reagents for the spectrophotometric determination of transition metals. In view of there the author has employed 2,4-dihydroxyacetyl1,4-hydroxybenzoichydrazone(2,4-DHAHB) as analytical spectrophotometric reagent for the determine of Co(II) and Ni(II) both the zero order and first and second derivative spectrophotometry.
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