PART- I
Chapter • I

INTRODUCTION
1.1. Trace Analysis

The adjectives macro and micro are used to refer to both to the size and amount of the constituent being determined. In the early days of analysis large size samples were used but with the demands of time and the progress of analytical techniques, determinations are made on samples in the milligram. Although the absolute amounts of substances dealt within macro and micro analysis differed by the factor 10 or 100, determinations below this limit were rarely run, partly because there was little demand and partly because such percentages were not readily determinable by the existing methods. The term trace was then used to designate a minute quantity of substance known to be present in the sample.

Determinations of constituents making up only a small proportion of the sample are frequently required today and it is desirable to define the term trace more exactly. The content of a major or minor constituent in a sample is ordinarily expressed in weight percentage. The same unit is often used for a trace constituent, but it is more convenient to use parts per million for contents below 0.001 percent.

The essential feature of a trace analysis is not the determination of a minute quantity of a substance but the determination of such a quantity in presence of an overwhelming quantity of other substances, which seriously affect the reaction of the trace constituent. A trace analysis has the characteristics of both macro and microanalysis. The final step in a trace analysis may be more micro than the usual microanalysis, in which 1 μg is usually the limit of accuracy sought.
A list of the methods, used in trace analysis would be a list of methods used in
general chemical analysis. The following list contains most of the methods in use at
present time.

1. Colourimetry, spectrophotometry and related methods like turbidimetry,
nephelometry and fluorimetry.

2. Optical spectrography (arc, spark and flame).

3. X-ray absorption and emission.

4. Radioactivation (neutron activation).

5. Mass spectrometry.

6. Polarography and other electrochemical methods.

7. Catalysis and induction.

8. Miscellaneous.

Some of these methods (Sr. No. 1,2,4) are both sensitive and applicable to
most elements while some are less sensitive and are of limited value in the ppm range.

The bulk of present day trace analyses are made by emission spectrography
and colourimetry. Spectrography can be applied to the determination of any element,
for some elements there are no satisfactory colourimetric methods and for others they
may not be sufficiently sensitive for use in trace analysis.

The introduction of foreign substances during the preparation of the sample
and in the course of the trace analysis may have more serious consequences in
spectrography than in any other type of analysis, and special attention must be paid to
this source of error.
Great care must be taken to prevent possible contamination of the sample through accidental introduction of metal from common articles of the laboratory like iron from ring stands, nickel from crucible tongs, copper and zinc from burners etc. If the sample requires shifting a silk blotting cloth must be used instead of a metal sieve. The possible introduction of some of the alloying elements of steel must be considered when a hardened steel mortar is used to crush hard materials such as silicates. The losses of a trace constituent may result from interaction with the material of the containing vessel. Loss by adsorption in glass vessels should be considered. Filter paper may adsorb metals as lead and copper from solutions, especially if these are neutral or only slightly acidic; inorganic filter media are in general preferable.

1.2. Colourimetric Methods of Analysis

The variation of the colour of a system with change in concentration of some components forms the basis of colourimetric analysis. The colour is usually due to the formation of a coloured compound by the addition of an appropriate reagent. The intensity of the colour may then be compared with that obtained by treating a known amount of the substance in the same manner.

Colourimetry is concerned with the determination of the concentration of a substance by measurement of the relative absorption of light with respect to a known concentration of the substance. In visual colourimetry natural or artificial white light is usually used as light source and determinations are usually made with a simple instrument termed as colourimeter. When the eye is replaced by a photoelectric cell
the instrument is termed as a photoelectric colourimeter. This is employed with light contained within a comparatively narrow range of wavelengths furnished by passing white light through filters that is materials in the from of plates of coloured glass, gelatin etc, transmitting only a limited spectral region.

In spectrophotometric analysis light of definite wavelengths extending to the ultraviolet region of the spectrum constitutes the source of light and thus necessitates the use of a more complicated and more expensive instrument, which is known as spectrophotometer.

1.3. Spectrophotometric Method of Analysis

The basis of Spectrophotometric method is the simple relationship between the absorption of radiation by a solution and the concentration of coloured species in the solution. In order to determine a species spectrophotometrically or colourimetrically it is usually converted into a coloured complex.

Spectrophotometric methods are remarkable for their versatility, sensitivity and precision. Thus, spectrophotometric methods are among the most precise instrumental methods of analysis. Several of the books dealing with spectrophotometry and spectrophotometric methods for determining the elements are classed among treatises of major importance 1-3.
1.4. Historical Outline

Attempts to utilize the colour of substances for their quantitative estimation are mentioned in reports dating back to ancient times and the middle ages. Certain writers ⁴ believe the origin of colourimetry to date from 1852, when Beer formulated the fundamental law of colourimetry.

Originally colourimetric determinations were done in colourimetric test tubes. In 1930 the first photoelectric colourimeters and spectrophotometers were introduced into laboratories. In the last 25 years the development of organic reagents and complex chemistry has entailed a tremendous increase in the number of spectrophotometric methods covering almost all the periodic table⁵-⁶.

At first the term colourimetry denoted a method of analysis in which elements were determined by comparison by estimation of the colours of sample and standard solutions. In photoelectric instruments the colour is neither measured nor compared; instead the fraction of the incident radiation that is absorbed by coloured solutions is measured.

1.5. Colour and Molecular Structure

Visible light represents a very small part of the electromagnetic spectrum and is generally considered to extend from 380 to 780 nm. A solution or object appears coloured when it transmits or absorbs only part of the radiation in the visible spectrum. The optical characteristic of the substance is its absorption spectrum.
There is a close relation between the colour of a substance and its electronic structure. A molecule or ion exhibits absorption in the visible or ultraviolet range, when radiation causes an electronic transition, raising the molecule from the ground state to an excited state. The production of a colour is connected with deformation of the normal electronic structure of the molecule. The colour of a molecule may be intensified by substituents called auxochromic groups. Examples of auxochromic groups, when substituted into phenyl, naphthyl, furyl or piperidyl rings are.

- OH, -NH₂, -SH, -CH₃, -Cl and -Br.

The colour-determining factor in a number of molecules is the introduction of conjugation of double bonds by means of electron donor and/or electron acceptor groups. Most transition metals with an incomplete d-electron subshell have chromophoric properties. These metals may occur in various oxidation states. They can give colour reactions with colourless reagents containing no chromophoric groups.

1.6. Absorption Laws

When a beam of radiant energy of intensity $I_o$ impinges upon a layer of coloured solution, some of this energy is absorbed ($I_a$), some is transmitted ($I_t$) and some is reflected ($I_r$).

$$I_o = I_a + I_t + I_r$$

Since measurements are always made with respect to a reference solution in a similar cell, $I_r$ is usually regarded as constant and neglected.

Absorption of radiation depends on the thickness of the coloured layer and on the concentration of the solution. In 1729, Bouguer established the relationship
between the absorption and the thickness of the absorbing medium. This relationship was formulated by Lambert in 1760 in a more accurate, mathematical way.

In 1852, Beer studied the relationship between the absorption of radiation and the concentration of the light-absorbing component of the solution.

When a parallel beam of monochromatic radiation of intensity $I$ impinge upon a layer of solutions of thickness $dl$, some radiant energy is absorbed. The fraction absorbed increases exponentially with linear increase in the layer thickness.

$$\frac{dl}{I} = -Kdl$$

Where $K$ is a constant and the minus sign denotes that the intensity of the radiation transmitted decreases as thickness of the layer increases.

Integration of this expression gives.

$$\ln \frac{Io}{It} = kl$$

Where $Io$ is initial intensity of the beam i.e. ($I = O$)

Conversion into Briggsian Logarithms gives,

$$\log \frac{Io}{It} = 0.434 \ln \frac{Io}{It} = 0.434 kI = kI = A$$

Where $k$ is a new constant and $A$ is called the absorbance. This formula i.e. Bauguer Lambert Law, represents the dependence of the absorption on the thickness of the layer.
If the concentration C of the absorbing species of the solution is doubled and
the thickness of the layer is reduced by a factor two, absorbance A will also remain
the same. The absorbance is therefore a function of the number of absorbing centers
in the light beam i.e. of the product c.l. and the equation for the absorbance can be
given the form,
\[ A = \log \frac{I_0}{I_t} = \varepsilon \cdot c \cdot l. \]

Where \( \varepsilon \) is a constant called as molar absorptivity, C is the concentration of coloured
species (mol/L) and l is the thickness of the absorbing layer (cm). When the
concentration is expressed in g/l, the constant is called the specific absorption
coefficient.

Usually the same optical path lengths are used for both the sample and
reference solutions in spectrophotometric measurements so that only the law, which
relates the absorption to the connection of the solute, is of practical significance.

When the coloured species obeys Beer's law a straight line passing through
the origin is obtained in the absorbance versus concentration plot. From a practical
point of view it is desirable that the solution should follow Beer's law for
concentration corresponding to absorbance up to at least 1.0. Deviations from Beer's
law may be produced by either chemical or physical cause. Chemical deviations
are caused by reactions induced in the solution as the concentration of species
increased. These may include condensations, polymerization, or hydrolysis.
When the solution of weak complex is diluted the complex dissociates which leads to
deviations from Beer's law at higher concentrations. When the extraction systems are used, there may be deviation from Beer’s law, caused by polymerization in the organic phase or the aqueous phase.

System in which stepwise formation of complex takes place does not obey Beer’s law. Deviations from Beer’s law may be produced by failure of the light sensitive element to respond strictly linearly to the radiation incident upon it. The optical medium must be homogeneous, turbid solutions give deviations from Beer’s law by scattering radiation.

Non-conformity to Beer’s law occurs in two colour systems where the reference solution absorbance is considerable at the wavelength chosen for measuring the absorbance of the complex solution. As the concentration of the complexed metal is increased, the concentration of the free reagent decreases in the solution, therefore its absorbance will be lower than that of the reference solution. If a large enough excess of the colour reagent is applied, this phenomenon does not occur.

1.7. Spectrophotometric Methods

In the standard curve method the relationship between the absorbance and the concentration of the substance to be determined is ascertained by using standard solutions and is expressed graphically. The standard curve is a straight line if Beer’s law is followed under experimental conditions. This method is generally used in spectrophotometric analysis.
Mahr 13-14 suggests the addition method for spectrophotometric determination. The element is determined from the change in absorbance when a known amount of the determinand is added. This method is more time consuming.

Differential spectrophotometry is based on measuring the absorbance of the test solution against a standard of accurately known concentration instead of a reagent blank or pure solvent. In this way the error in measurement is confined to the difference in the two concentrations and so can be minimized.

There are several variants of differential spectrophotometry15-16. The measurement error is much smaller than in ordinary spectrophotometry17-19 and may be as low as 0.2 %. In differential spectrophotometry it is necessary to take heed of some sources of error. Particular care is required in the preparation of the standard solutions, and for maintaining temperature. In differential spectrophotometry the absorbance is usually high and a wider slit width is necessary to permit sufficient light to be transmitted to the detector 20.

Spectrophotometric titration21-26 involves monitoring the absorbance during titration of the sample solution. This method can be applied whether Beer’s law is obeyed or not, provided that near the end point there is an almost linear relation between the absorbance and the concentration of the light absorbing compound in the solution. The species to be monitored can be a reactant, a product or an indicator. The titration is represented graphically by two intersecting lines in a plot of absorbance against volume of titrant added. In order to find end point it is enough to
determine two points before and after it. The titration is carried out either at a definite wavelength or with a suitable filter.

Spectrophotometric titration method is especially useful when the end point is difficult to decide visually. Complex formation, redox, neutralization and precipitation reactions are all used with or without indicators. Extraction systems have been used. When precipitation reactions are used, a collimating slit should be added to the apparatus to avoid errors caused by back scatter of radiation by the precipitate.

Automated spectrophotometry is of ever increasing significance in chemical analysis. Automation is applied to spectrophotometric methods for routine analyses and for on line control in industrial processes. Typical examples of this method are the determination of chloride, nitrate and iron in water, silicon, phosphorus and manganese in steel, trace metal contaminants in a wide range of chemicals and a major components in nickel, cobalt, iron and manganese oxide mixture.

1.8. Sensitivity of Spectrophotometric Methods

Sensitivity refers to the slope of the calibration curve, but is frequently used to mean the least determinable concentration or amount of the species of interest.

The objective numerical expression of the sensitivity of spectrophotometric methods is the molar absorptivity (ε) at the wavelength (λ_max) of maximum absorbance of the coloured species.

\[ \varepsilon = \frac{A}{c \cdot l} \]
where \( A \) is the absorbance, \( c \) is concentration of the coloured species (mole/L), and \( l \) is the light path length. If \( l \) is in cm, the molar absorptivity \( (\varepsilon) \) is expressed in \( 1 \text{ mol}^{-1} \cdot \text{cm}^{-1} \).

Molar absorptivity was formerly called the molar absorption coefficient or molar extinction coefficient. Molar absorptivity should be expressed so as to take into account the number of significant digits, i.e. the precision of the measurements for sensitive spectrophotometric methods \( \varepsilon \) is \( > 1 \times 10^4 \text{ L mol}^{-1} \cdot \text{cm}^{-1} \) and values of \( \varepsilon \) below \( 1 \times 10^3 \text{ L mol}^{-1} \cdot \text{cm}^{-1} \) correspond to less sensitive methods. The molar absorptivity cannot exceed \( \approx 1.5 \times 10^5 \text{ L mol}^{-1} \cdot \text{cm}^{-1} \) according to quantum theory.

It is convenient to express and compare the sensitivities of spectrophotometric methods in terms of specific absorptivity \( (a) \). This is obtained by dividing \( \varepsilon \) by the atomic weight of the element and by 1000.

\[
a = \frac{\varepsilon}{\text{At. Wt.} \times 1000}
\]

The value 'a' (in ml. g\(^{-1}\), cm\(^{-1}\)) corresponds to the absorbance of a 1 \( \mu \text{g} / \text{ml} \) solution of the determinand in a curette with an optical path length of 1 cm.

The sensitivity of spectrophotometric methods is often expressed in terms of the expression given by Sandell, which represents the number of micrograms of the determinand per ml of solution having an absorbance of 0.001 for a path length of 1 cm. The sensitivity (S) according to Sandell is expressed in \( \mu \text{g} \cdot \text{cm}^{-2} \).

The sensitivity of spectrophotometric measurements depends very much on the monochromatacity of the radiation. The molar absorptivity diminishes as the bandwidth increases. In the determination of \( \varepsilon \) the absorbance measured should be
within the range over which the coloured system conforms to Beers law and within
the range of values for which the measurement error is minimal.

It is easiest to determine $\varepsilon$ when the spectrophotometric reagent has practically
zero absorption at $\lambda_{\text{max}}$ for the complex and only one coloured complex is formed in
the system. If the complex has low stability a large excess of reagent is used to shift
the equilibrium. Determination of the molar absorptivity when the reagent also
absorbs at $\lambda_{\text{max}}$ for the complex is more difficult, but if only one stable coloured
complex is formed, the absorbance can be measured against a reference solution in
which the reagent concentration is the same as the concentration of uncombined
reagent in the test solution.

There are computational and graphical methods for determining $\varepsilon$ when the
coloured reagent absorbs at $\lambda_{\text{max}}$ of the complex. Both methods give consistent
results.

If more than one coloured complex is formed that absorbs in the same region,
it is necessary to add a very large excess of reagent in order to form the highest
complex completely and to determine the absorption spectrum and hence its $\varepsilon$ values
at the wavelengths of interest.

The determination of $\varepsilon$ in extraction spectrophotometric methods is generally
simple. The extraction usually involves a single complex. Extraction often enhances
the sensitivity of the method.

In some spectrophotometric methods sensitivity depends on the quality of the
reagent used particularly with reagents, which are natural products. In the case of
certain synthetic organic reagents differences in sensitivity have also been found. Differences in sensitivity also result from the presence of foreign substances in the preparation.

The lowest concentration that can be determined spectrophotometrically\textsuperscript{38-39} can be calculated from the fundamental formula \( A = e \cdot c \cdot l \). Trace concentrations smaller than 10\(^{-4}\) % are below the sensitivities of most spectrophotometric methods where the colour is developed directly in the aqueous phase. In order to determine them spectrophotometrically either an extraction procedure or preconcentration step is necessary.

1.9. Precision and Accuracy of Spectrophotometric Methods

In analytical chemistry the term precision is used to indicate reproducibility, scatter, and consistency of results. The precision of spectrophotometric methods \textsuperscript{17,40-43} depends on the concentration of the determinand and on the measuring technique adopted. Visual methods give results with a precision of 5-10 %. The precision of the objective photoelectric method is higher and varies from 0.5 to 2 % under suitable measuring conditions.

In the photoelectric methods the measurement error is of importance for precision. When intensely coloured solutions are being measured only an insignificant part of the radiation is transmitted and on the logarithmic absorbance scale the graduations are so close that the reading error is very high.

Errors connected with the measurement of absorbance are usually smaller than those associated with the chemical operations in the determination. In some
spectrophotometric methods the colour reaction is not reproducible. In others the colour produced is not stable with respect to time, and the absorbance must be measured at a fixed time from the start of the colour reaction. In some systems temperature variations as small as 3 to 5 °C can cause differences in colour. Some colour reactions are very sensitive to pH changes. A change of as little as 0.1 in the pH may sometimes cause errors up to 5 %.

The overall error of the determination is the summation of the errors committed at each stage of the procedure like in sampling, dissolution of the sample, preconcentration, separation of elements and spectrophotometric determination. In trace analysis an accurate blank determination is also important. The influence of the blank on the accuracy increases as the determined concentration decreases.

1.10. Selectivity of Spectrophotometric Methods

According to the definitions recommended by the Analytical Chemistry Division of Pure and Applied Chemistry, a reagent, which reacts with a limited number of elements, is considered to be selective and a reagent may be called specific if it gives a reaction with only one element in certain circumstances. Accordingly selective and specific spectrophotometric methods were developed.

The selectivity of colour reactions and corresponding spectrophotometric methods depends on the nature of the reagent used, the oxidation state of the element, the pH of the medium and the nature of complexing agents used to mask interfering ions. In spite of use of all these factors some ions can still interfere in a
determination, then the species to be determined has to be separated from the interfering species or vice-versa.

A change in oxidation state of certain ions is enough to prevent their reaction with certain reagents. In the determination of niobium by thiocyanate method, for example, iron does not interfere if reduced to Fe (II). Change in oxidation state is rather seldom used to enhance the selectivity of spectrophotometric reactions. The selectivity of most methods is improved by choosing a suitable pH for the reaction medium. The nature of the reagent used has a specific influence in reactions with particular elements, but the general tendency remains the same.

Increased selectivity of spectrophotometric methods is mainly obtained by masking the interfering ions. The masking consists in transforming the interfering ion into a stable complex with a complex forming agent so that it can neither react with the spectrophotometric reagent, nor otherwise interfere in the colour reaction of interest.

High selectivity is obtainable by a suitable combination of masking agent and pH. The effective stability of complexes is not constant but varies with the pH and other parameters. The release of an ion from the complex formed as a result of masking reaction is called demasking. In discussion of the selectivity of spectrophotometric methods, mention should also be made of simultaneous determination of two coloured complexes by measuring the absorbances at two different wavelengths.
1.11. Solvent Extraction

Liquid-liquid extraction is a technique in which a solution (aqueous) is brought into contact with a second solvent (organic) essentially immiscible with the first, in order to bring about a transfer of one or more solutes into the second solvent. In many cases separation may be affected by shaking in a separatory funnel. The technique is usually applicable to trace level concentrations and large amounts of materials.

To understand the fundamental principles of extraction, the various terms used for expressing the effectiveness of a separation must first be considered for a solute ‘A’ distributed between two immiscible phases a and b. The Nernst distribution law states that, provided its molecular state is the same in both liquids and that the temperature is constant,

\[
\frac{[A]_a}{[A]_b} = K_D
\]

Where \( K_D \) is a constant known as the distribution coefficient. In the practical applications of solvent extraction we are interested primarily in the fraction of the total solute in one or other phase, regardless of its mode of dissociation, association or interaction with other dissolved species.

It is well known that hydrated inorganic salts tend to be more soluble in water than in organic solvents, whereas organic substances tend to be more soluble in organic solvents than in water unless they incorporate a sufficient number of hydroxyl, sulphonic or other hydrophilic groupings. In the solvent extraction analysis
for metals are concerned with methods by which the water solubility of inorganic cations may be masked by interaction with appropriate organic reagents.

Ionic compounds would not be expected to extract into organic solvents from aqueous solution because of the large loss in electrostatic salvation energy. The most obvious way to make an aqueous ionic species extractable is to neutralize its charge. This can be done by formation of a neutral metal chelate complex or by ion association.

In chelation complexes the central metal ion co-ordinates with a polyfunctional organic base to form a stable ring compound. Generally chelate formation depends upon the basic strength of the chelating group and the nature of the donor atoms in the chelating agents.

Solvent extraction is becoming more and more important in inorganic and analytical chemistry.

Transport of materials from one phase to another is the most fundamental procedure for the separation of a chemical species from other coexisting components. Solvent extraction usually permits much simpler and cleaner separation of materials at both macro and trace concentrations.

Solvent extraction has been a fundamental technique of organic chemistry. The solvent extraction of some inorganic compounds was known in the nineteenth century. The first such example was the extraction of uranyl nitrate into diethyl ether reported in 1842 by Peligot. In 1892 Rothe and Hanroît extracted iron in hydrochloric acid with diethylether. This method was then applied to the separation of this element
from many other metal ions. A quantitative understanding of liquid-liquid distribution equilibria was first introduced in 1872 by Bertbelot and Jungfleisch and elucidated thermodynamically in 1891 by Nerst. The distribution law was applied to the determination of chemical equilibria of various solutes in solutions as early as about 1900. The solvent extraction technique was almost completely ignored until the method for the extraction of metal ions as organophilic chelate complexes were discovered.

In 1925 dithiozone was introduced by Fischer as a precipitant of some metal ions forming stable chelate complexes. The extraction of metal ions as chelate complexes with cupferron or with dimethylglyoxime was also reported in 1930 and that with 1-nitroso-2 naphthol or 8- hydroxyquinoline was reported in the early 1940. These studies expanded the possibilities of solvent extraction methods although the chemical knowledge and the variety of reagents were still limited.

Solvent extraction studies have been reviewed by a number of authors. After early publications Morrison and Freiser wrote a comprehensive monograph on solvent extraction in analytical chemistry. The solvent extraction of metal chelate complexes was reviewed by Stray. The ion exchange of metal complexes and their solvent extraction were discussed by Marcus and Kerets and the analytical use of solvent extraction of metals was published in book form by De et al.
One of the reviews concerned with the solvent extraction of inorganic substances; was written by Marcus 60. Various reports on the fundamentals and application of solvent extraction chemistry presented at the International conference on solvent extraction chemistry have been published 61-64. The application of solvent extraction methods has also been reviewed by some authors like applications to solution chemistry by Rosotti and Rosotti 65, and to analytical chemistry by Sandell 66, Ringbom 67 and Korkisch 68. Further more a series of reviews on solvent extraction in various fields has been published 69. The applications to analytical chemistry are comprehensively reviewed by the Journal of Analytical chemistry 70-80.

Recently, solvent extraction technique was used for the determination of metals such as Bismuth 81, Gold 82,83 and platinum metals 84 by using pyrimidine thiol, Rhodium 85 by using 1-(4' -bromophenyl)-4,4,6-trimethyl-(1H,4H)-2 pyrimidinethiol. Trivalent lanthanides 86 are extracted with amides, Copper 87 was extracted from chalcopyrite concentrates, Nickel 88 was recovered from nickel plating baths, micro amounts of Ir (III) 89 was extracted with 3-hydroxy-2-methyl-1-phenyl-4-pyridone was reported and Te (IV) 90 with thiol was also reported.

Removal of Bi, Cd, Co, Cu, Fe, Ni, Pb, and Zn from aqueous medium with bis (2-ethylhexyl) phosphoric acid by using solvent extraction was reported by Huynh 91. Rhodium was extracted from hydrochloric acid solutions containing Tin 92. Copper recovery by using solvent extraction was reported by Koyama 93. Solvent extraction of lanthanides with N, N- dimethyl-N,N-diphenylmalonamide and -3,6-dioxoactanedimide was reported by Narita 94. Extraction of Am (III) and
Lanthanide (III) ions from nitric acid solutions using N, N'-dimethyl-N, N'-diphenylpyridine-2, 6- dicarboxyamide was reported by Shimada 95.

Equilibria study of Y (III) and Eu (III) by using solvent extraction was reported by Fu and Tanaka 96. Selenium was determined with a chromogenic reagent 97.

Application to solvent extraction technology to PCB (polychlorinated biphenyl) contaminated soil and chemical/bioassy monitoring was reported by Takigami et al 98. In short liquid liquid extraction is widely used in the treatment of relatively concentrated aqueous solutions but is less suitable for processing large volumes of solution containing trace amounts of metal due to solvent solubility losses and third phase formation 99-101.
1.12. References


66. Sandell E.B. "Colourimetric Determination of Traces of Metals", Ed.3, Inter


68. Korkisch J., "Modern Methods for the Separation of Rarer Metal Ions",


