Lecture No. 7

UV-Vis SPECTROPHOTOMETRY (COLORIMETRY)

by

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PRINCIPLE AND APPLICATION OF THE SPECTROPHOTOMETRY FOR THE ANALYSIS OF METALLURGICAL SAMPLES

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The spectrophotometric method is in use over a period of many years with numerous contributions from many disciplines. At present, the technique has attained such a state of sophistication and maturity that it is one of the most widely used methods of chemical analysis. This paper covers (i) theoretical concepts underlying these methods (ii) essential characteristics of instrumentations (iii) the general methodology and (iv) its application to metallurgical analysis specially for minerals and metallurgical samples.

INTRODUCTION

The molecular absorption spectrophotometry in the visible and U.V spectral ranges always plays a very important role in the quantitative analysis, for their versatility, sensitivity and precision. In the last 25 years the development of organic reagents and of complex chemistry has entailed the tremendous increase in the number of spectrophotometric methods[1-3] for the determination of large number of elements over a wide range of concentration from macroquantities (1-50%; specially by differential methods[4-8] to traces (10^{-8} - 10^{-6}%) after preconcentration and 10^{-3} - 10^{-7}% without special preconcentration.

Briefly, the spectrophotometric methods are applicable in general to the following problems:

(a)   Quantitative analysis for certain cations, anions and organic groups in concentration ranging from traces to appreciable.

(b)   Measurement of pH, dissociation, reaction rate etc.

(c)   Investigation of molecular structure.

(d)   Analysis of mixtures.

Several of the books dealing with spectrophotometry and spectrometric methods for determining the elements are classed among the treatises of major importance[7-10].

Theoretical Concept of Spectrophotometry

There are two fundamental laws which govern the absorption of monochromatic light by homogeneous transparent media, which are (i) Bouguer-Lambert law and (ii) Beer's law.

Bouguer-Lambert law:

In 1729; Bouguer established the relationship between the absorption and thickness of the absorbing medium. The relationship was formulated by Lambert in 1760 in a more accurate and mathematical way. It states that for a given thickness of solution of a substance the proportion of light that can be absorbed in a constant, being independent of the intensity of incident light.

Beer's law:

Beer's law put forth a quantitative treatment of the absorption of radiant energy by matter. When a beam of radiant energy falls upon a substance many changes may occur. A portion of the radiant energy may be reflected, refracted or diffracted. Scattering may occur by particulate suspended matter (Fig.1). The radiant energy may be absorbed entirely or in part.

In other words it can be said that Beer established the relationship between the absorption of radiation and the
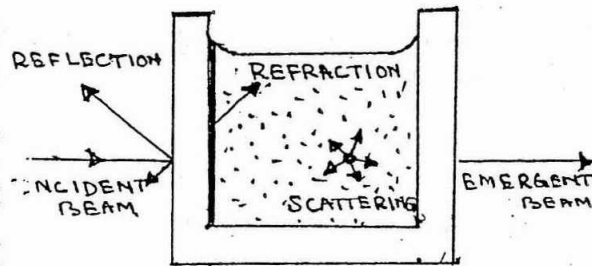
Fig.1: Incident radiation falling on a system

and the concentration of the light absorbing components of
the solution, that is the absorption of light is directly
proportional to the concentration of the solution through
which the light passes.

The combined law is generally referred to as Beer's law
and expressed mathematically as

$$A = abc \qquad\qquad .. \quad (1)$$

where A = absorbance
      a = absorptivity
      b = light pathlength
      c = concentration of the coloured species

Deviation from Beer's Law

From the statement of Beer's law and prediction of
equation (1), it is expected that with the change of concen-
tration of absorbing medium, the absorbance will accordingly

vary so if we plot absorbance A, against concentration, a
straight line should be obtained passing through the origin
(Fig.2). In practice it has been observed that the absorbance
curve (Fig.3) may sometimes deviate from the expected one
with concentration variation and an apparent failure of Beer's
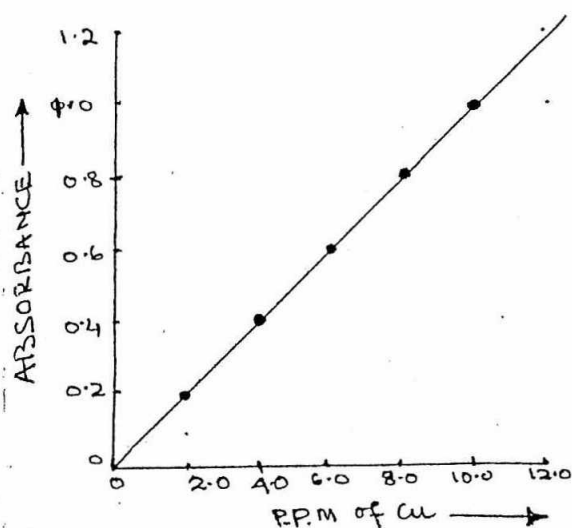

Fig.2: Plots testing for
        conformity to
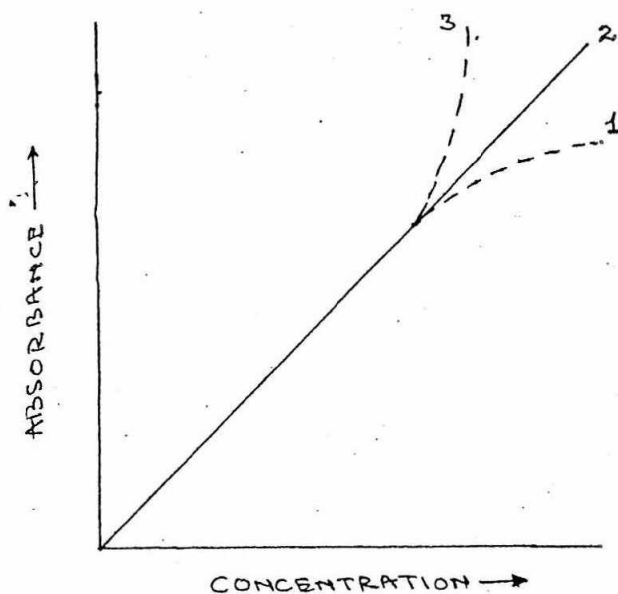   Beer's law

Fig 3: Deviation from Beer's law
        (a) Negative deviation,
        (b) follows Beer's law,
        (c) positive deviation

law may ensure. Deviations from the law are reported as posi-
tive or negative according to whether the resultant curve is
concave upward and concave downword. These deviations may be
attributed to interaction between absorbing molecules with
one another. Polymerisation might be the casual factor for
such deviation.

Standard Deviation and Coefficient of Variation

When one measures a quantity, he takes full care of the
instrument, method and personal precision. It has been
observed that although we may take possible precautions, the
determination still differ among themselves to some extent.

We may thus have the average value but this may not be the true value, being only the most probable value.

Accuracy of a measurement can be known from the absolute error of the determination. Absolute error is the difference between the true value and the observed value. The relative error is obtained by dividing absolute error by the true value. It is expressed in percentage or parts.

Precision of an experiment may be defined as the agreement between the number of measurements of the same quantity. One of the ways for measurement of precision is from mean deviation or relative deviation. Mean deviation is obtained first by calculating the arthmatical mean of the results and then finding the deviation of each individual measurement from the arithematic mean and lastly dividing the sum of the deviations (taking no account of sign) by the total number of measurements. The relative mean deviation is the mean deviation divided by arthematic mean. This is also expressed in percent or part per thousand.

Precision in U.V and Visible Spectrophotometry

Random error cames from the instrument, e.g instability and growing old of the source, instability of the electronic or electrical schemes, the instrument noise, the nonlinear response of the detector, the scattered light etc, from the accessories such as cells or from the subject [error of scale (absence or wavelength) readings, incorrect evaluation of the balank etc]. Such errores can be negligible using modern spectrophotometers and comparing them to deviations coming from the chemical or photochemical reactions.

A SYSTEMATIC APPROACH TO SPECTROPHOTOMETRIC DETERMINATION OF METAL IONS BY ORGANIC REAGENTS

Keeping the facts in mind we can prepare a reagent which will be effective for spectrophotometric determination of

metal ions. Here a discussion will be made regarding how the reagent could be systematically applied for such analytical purpose. After preparation of the pure reagent, we firstly note its solubility in various solvents, effect of heat and light upon it, its stability towards acids and bases and the duration it can be preserved (in normal or varying the condition). We always prefer that reagents which can be prepared easily with a high percentile yield, sensitive towards reacting ions and stable in normal condition. Next, after dissolving the reagent in a suitable solvent we test it qualitatively for its possible colour reactions with different ions at various acidity and alkalinity. Such a study will reveal whether the reagent is specific for any ion or not. After this simple study, we may proceed to employ the reagent for quantitative evaluation of those ions we are interested. For such a quantitation we usually are to find out the followings:

(a) Wavelength at which the complex has maximum absorption (λ max). This point may be obtained by plotting absorbances against different wavelengths (absorbance curve).

(b) The acidity or alkalinity range of the colour (pH range). This point may be obtained by obtaining absorbants against pH.

(c) Beer's law range.

(d) Effect of reagent.

(e) Effects of temperature and time.

(f) Effect of various other ions or the colour systems etc.

ESSENTIAL CHARACTERISTICS OF INSTRUMENTATION

There are four essential components which is found in common spectrophotometer:

1. **Source of radiant energy:** A tungsten filament lamp is widely used for the visible (400-800 nm) and near infra-red region (850-3000 nm), the deuterium

(hydrogen) discharge lamp is used in ultraviolet region (200-400 nm).

2. **Monochromater:** This permits the selection of radiant energy of the desired wave-length. A monochromater consist of an entrance and exist slits and a dispersive device to separate a continuous spectrum into its constituent wave-lengths. Here the dispersive devices are prisms or diffraction gratings.

3. **Sample holder:** It is very important that the cells are positioned in a reproducible manner and the cells used in a series of measurements be matured in respect to a spectral transmission characteristics. For the precision work it is prefered that entrance and exists sides be plane, parallel surface.

4. **Photometer:** This detects the transmitted radiant energy and produces an electrical signal proportional to the radiant power of the light beam.
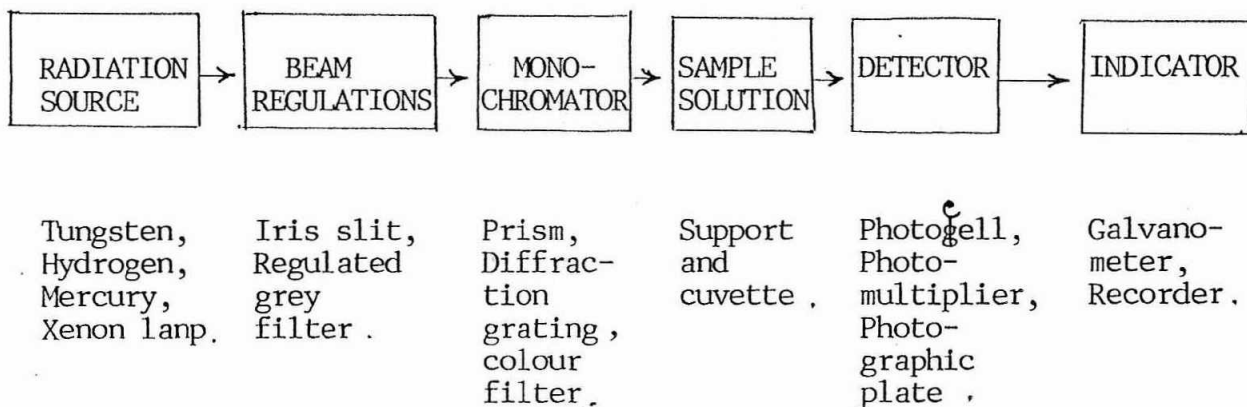
RADIATION SOURCE	→	BEAM REGULATIONS	→	MONO-CHROMATOR	→	SAMPLE SOLUTION	→	DETECTOR	→	INDICATOR
Tungsten, Hydrogen, Mercury, Xenon lanp.		Iris slit, Regulated grey filter .		Prism, Diffraction grating, colour filter.		Support and cuvette .		Photocell, Photomultiplier, Photographic plate ,		Galvanometer, Recorder .

Fig.4: Block diagram of spectrophotometer

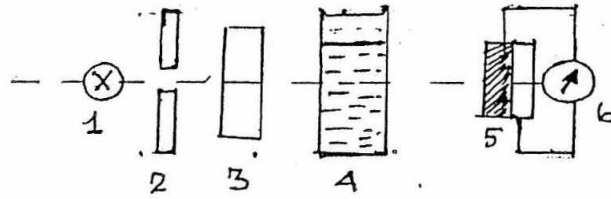Spectrophotometers are divided into single-beam and double-beam instruments.

Fig.5: Scheme of single-beam spectrophotometer
1 lamp, 2 iris, 3 monochromator or filter,
4 sample or reference solutions,
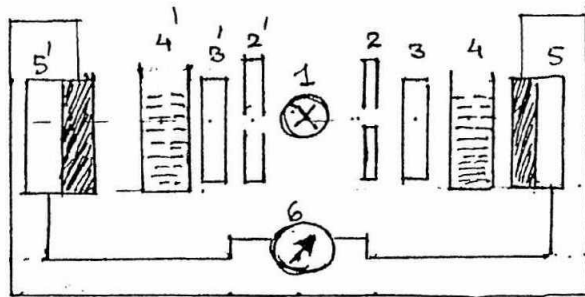5 photocell, 6 galvanometer

Fig.6: Scheme of double-beam spectrophotometer
1 lamp, 2 and 2' irises, 3 and 3' mono-
chromators or filters, 4 sample solutions,
4' reference solution, 5 and 5' photo-
cells, 6 galvanometer

In the single beam instrument presented in Fig.5 the reference solution and the sample solution are inserted successively into the radiation beam, and the radiant powers transmitted are measured.

In the double-beam instrument in Fig.6 the beam of radiation is divided into two parallel beams of which one passes through the reference solution and the other traverses the sample solution. Each beam impinges on a separate detector and a galvanometer indicates the difference in the current generated in the two detecters.

GENERAL METHODOLOGY

(i) **Sample preparation**: Since most of the samples of metallurgical interest are solids, the preparation of a coloured solution suitable for photometric measurement constitutes an important step in the analytical procedure. During dissolution care must taken not to introduce any unwanted metals from the reagents being used. Almost all photometric methods for the determination of metals depends on oxidation, reduction or chelation reactions for the development of suitable colour. The acidity or pH is often critical for the maximum development of colour. Other factors which accounts for the development of colour include amount and concentration of reagents, order of addition of reagents, temperature, time and ionic strength.

(ii) **Removal of interference**: Although very often reaction are specific for a particular substance many reactions are quite selective and can be rendered selective through the introduction of masking agents[11], control of pH, adjustment of oxidation state or by prior removal of interferents using solvent extraction techniques[12]. It is often necessary to specify that the colour comparison be

made within a definite period of time and it is
always advisable to prepare standards and unknowns
on the definite time schedule. When extraneous
colour bodies are present the standards should
match the composition of the sample solution.

(iii) **Measurement of the system:** The next step after the
sample preparation and removal of interfering ions,
is the measurement of absorbance at specific wave-
length. The selection of the appropriate wave-
length of measurement should be based on a sound
knowledge in the chemical method and the instrument
being used. But in general the wave-lengths are
taken at maximum absorbance for the prepared solu-
tion. However, there are conditions under which
measurement at the absorbance maximum is not
recommended.

Spectrometric data are commonly presented in graphi-
cal form by (1) plotting either absorbance or trans-
mittance vs wave-length (Fig.7) to obtain the charac-
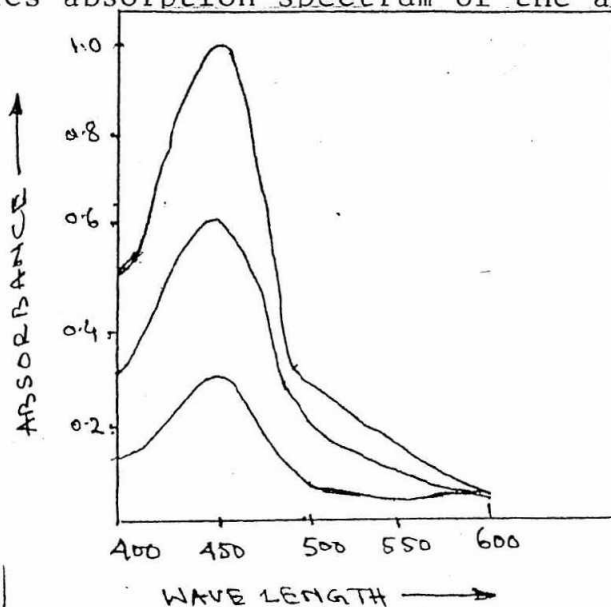teristics absorption spectrum of the absorber and

Fig.7: Typical spectral transmittance curve

(2) plotting absorbance vs concentration (Fig.3) in
order to obtain calibration graph. The common method

of using the spectrophotometer requires the construc-
tion of standard curve for constituents being deter-
mined. For this purpose suitable quantities of the
constituents are taken and treated exactly the same
way as the sample solution for the development of
the colour and the measurement of the absorbance at
the optimum wavelength. The absorbance is plotted
against the concentration of the constituent. A
linearship for absorbance vs concentration plot
indicates confirming Beer's law (Fig.3). If there
is no complications due to polychromacity of the light,
this curve may then be used in future determination
of the constituents under the same condition. From
the practical point of view this desirable that the
solution should follow Beer's law concentration
corresponding to absorbance upto at least 1.0.

(iv)   **Sources of error:** It is impossible to eliminate
errors in chemical analysis totally, but is advant-
ageous to be able at least to determine the magnitude
or orientation of these errors, inorder to have more
definite, concrete knowledge of the reliability of
our results.

Most errors in spectrophotometric analysis can be
attributed either to (a) the nature of the chemical
system prepared for measurement, (b) the operational
characteristics of the instrument being used and (c)
faulty technique. It is no longer sufficient to-day
for an analyst or chemist to be able to carryout an
analysis reliably according to a given procedure. He
must be able to select a correct procedure and it is
often required of him to be able to assess the result
obtained. The absorption system should be homogenous
coloured solution, free of turbidity. The stability
of the system should be sufficient to permit photo-
metric measurements within a reasonable period of
time. Certain metal chelates exhibit fluorescence
which can result in the diminution of the absorbance

value if the fluorescence emission overlaps the wave-
length of photometric measurement. Instrumental
errors depends on the specific instrument being used
and the manner it is being operated. The spectral
slit width effect is related to the spectral emittance
curve of the source and the resolving power of the
monochrometer.

Errors in technique include use of unclean or non-
matched absorption cells, failure to adjust instru-
ment for 0%, transmittance measurement outside optimum
concentration range, use of wide range of slit widths,
when measuring a narrow absorbance maximum, failure
of instruments to achieve stability, misalignment of
source, selection of improper filter and wave-lengths,
carelessness in the addition of reagents in the
development of the coloured system, dilution errors
and volumatric changes due to temperature.

APPLICATIONS

The application of spectrophotometry to chemical and
metallurgical analysis are, however, exceedingly numerous.
Attention should be called to some of the standard texts on
chemical analysis. Several of the books dealing with spectro-
photometry and spectrophotometric methods for determining the
elements are classed among treatise of major importance[7-10,13]

Metals

Over 170 different spectrophotometric methods for the
determination of 46 metals, exclusive of the rare-earth
elements, have been compiled in a tabular form[14]. Many of
these methods are discussed critically in Sandell's treaties[7]
and additional applications of these methods are cited by
Snell and Snell[8].

Most spectrophotometric methods for the determination
of metals are based either on oxidation, reduction or Chela-
tion reactions. The oxidation of Mn(II) to Mn(VII) with
periodate and the determination of Cr as Cr(VI) are examples
of oxidation reaction. Estimation of molybdenum is done by
reducing Mo(VI) to Mo(V). Chelating agents which form metal
chelates are extensively used in spectrophotometric analysis,
because of the high absorptivity of these compounds. A
considerable number of metals and metalloids, can be sepa-
rated by distillation from aqueous solution after conversion
into suitable compounds.

Non-metals

Spectrophotometric methods for most of the non-metals
and the application of these methods to the analysis of
numerous metallurgical samples have been discussed[14]. Non-
metallic elements such as phosphorus and silicon form yellow
hetropoly complexes which can be measured photometrically
and these complexes can be reduced to produce hetropoly blues
which have unusually high absorptivity values. Quinalizarin
forms a purplish - coloured solution with boron which help
it in the determination of the elements in steel[15]. The
methylene blue method has been used to determine sulphur in
iron alloys[16-18]. The determination of combined carbon in
steel and cast iron by difference method has been dealt in
detail by Haywood and Word[13].

Advantages Over Other Colorimeters

The main advantages over the other colorimeters are
(i) Large personal errors can be avoided, (ii) Since many
common reagents are not specific, failure to recognize this
fact may lead to a systematic and undetected error in the
colorimeter which can be eliminated by spectrophotometer,
(iii) It permits selections of the proper wave-length for
comparison and it is applicable to the simultaneous

determination of more than one component, (iv) It is possible
to avoid or minimize the effect of foreign coloured sub-
stances by working at suitable wave-length, and (v) Higher
precision can be obtained in photoelectric spectrophoto-
metry than in ordinary colorimetry.

SUMMARY AND DISCUSSION

The problems faced in the chemical and metallurgical
industries necessitate rapid and at the same time accurate,
reliable analytical control of the entire course of produc-
tion processes, starting from raw materials through inter-
mediate production upto the finished product. So owing to
the ease, sensitivity, rapidity suitability for the deter-
minations of micro amount of metals and non-metals, minimal
expenditure for instrumentation and operation spectrophoto-
metry is now widely used in industrial analytical laboratories
and research investigations.

Keeping all these points in view, it is suggested that
selection of spectrophotometric method for a particular
determinations depends on many factors such as:

(1) Concentration of desired constituents in sample

(2) Nature and amount of other elements in sample

(3) Amount of sample

(4) Accuracy required

(5) Number of samples to be analysed

(6) Availability of instruments for alternative
     methods of analysis and its cost in terms
     of man-hours.

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