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*colorimetric  
determination  
of  
elements*

# COLORIMETRIC DETERMINATION OF ELEMENTS

PRINCIPLES AND METHODS

by

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## PREFACE

This new edition was undertaken because of the rapid strides which have been made in colorimetric determinations since the first edition was published. As before, it is intended for use by the practising chemist.

In the first part will be found an account of the principles necessary for full understanding of the method. Also included are accounts of the newer separation methods, particularly those of extraction and ion-exchange.

Emphasis has been given throughout to the most accurate estimations which are now possible through the development of differential methods using double-beam spectrophotometers. The growing importance of spectrophotometric titrations has also been stressed.

The second part of the book deals with the actual estimation of the more important elements. Methods of separation and selected estimation procedures are given for each one. This section of the work is not simply a compilation of well-known methods; indeed, it incorporates not only new methods selected and developed in our own laboratories, but also experience gained in the following organisations with which the author is connected: Commission des Méthodes d'Analyse du Commissariat à l'Energie Atomique, Association Française de Normalisation, Sections de Chimie Analytique de la Société Chimique de France, Société de Chimie Industrielle, etc. Numerous discussions with industrial laboratories either directly or through former pupils have also played their part in the selection of methods, although not all those quoted have been subjected to this treatment. On the other hand, many elements of particular interest at the present time [uranium, thorium, titanium, zirconium, niobium, tantalum, boron, beryllium etc.] have been especially studied, both in a general way and in the determination of small traces.

I am conscious of the fact that many imperfections must be present in both sections of the book, and will greatly welcome any comments or criticisms which the reader may send to me.

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*Paris*  
*December 1963*

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*Part I*

**Theoretical Background**





## Characteristics of the colorimetric method

The names absorptiometry or absorption spectrophotometry refer to a very widely applicable method, in which a beam of light of a given wavelength is analyzed after passing through the substance to be determined. The latter is generally a solution, but may also be a gas or even a solid. The concentration of the absorbing substance is deduced from the proportion of the luminous intensity absorbed by the solution.

The spectral ranges covered by various radiations are given below:

$10^{-3} \text{ m}\mu$	cosmic rays
$10^{-2}$ to $10^{-1} \text{ m}\mu$	$\gamma$ rays
$0.1 \text{ m}\mu$	x rays
$200 \text{ m}\mu$	} ultraviolet
$400 \text{ m}\mu$	
	} visible
$800 \text{ m}\mu$	
	} infrared
$100 \mu$	
$1 \text{ cm}$	} centimetre and radio waves
$10^4 \text{ m}$	

We shall here particularly concern ourselves with the methods relating to that part of the spectrum which extends from ultraviolet ( $220 \text{ m}\mu$ ) to the beginning of infrared ( $1 \mu$ ), as the above regions are of interest in the case of inorganic compounds. The same principles are applicable, however, with some variations, to other parts of the spectrum, and particularly to the infrared region.

The method is called absorptiometry, absorption photometry, spectrophotometry, and more usually, although improperly, colorimetry. (In actual fact the term 'colorimetry' denotes the methods of analysis, specification, and description of colours). The term 'colorimetric methods of analysis' can however be used without ambiguity.

Colorimetric methods of analysis are at present undergoing considerable development and may, assuming a judicious choice of conditions, be applied to a great number of estimations with adequate accuracy. At the same time, a wide and growing variety of superior quality instruments is now becoming available commercially.

*The field of application and advantages of the method.* Formerly, 'colorimetry' was almost exclusively confined to the estimation of trace amounts, owing to its poor degree of accuracy. At the present time, however, improved methods of instrumentation and the use of the differential method sometimes permit an accuracy to be obtained which is comparable with, or better, than that of current volumetric methods (0.2–0.5%). Absorptiometry has acquired an even greater importance than volumetric estimation, and is today the most important method of analysis. Its main advantages are the following:

(a) The method is capable of very general application; thus if the substance to be determined exhibits only low absorption, suitable reagents may be added to form compounds of higher absorbing power.

(b) The method may be made extremely sensitive, particularly if organic reagents are used. The estimation of trace amounts is now carried out by this method more frequently than by any other.

(c) The method can be extremely rapid since direct measurements may be carried out without the necessity of using standardized solutions and owing to the simplicity of the experimental procedure. Moreover, separations can be simplified or avoided, since to eliminate the effect of interfering ions, all factors which are used in the chemical manipulation of solutions are also available here: selection of reagent, oxidation-reduction, adjustment of pH, formation of complexes, and the use of organic solvents, in addition to a supplementary factor, *i.e.* selection of the wavelength used.

(d) Finally, the method lays open a very important possibility. We shall see that, by comparison with a solution containing only the interfering materials ('blank test'), a material can very often be estimated in the presence of other absorbing substances.

In addition, 'colorimetry' permits a reaction to be followed and its equivalence point to be determined (see *Colorimetric Titrations*, discussed in Chapter 7).

## Chapter I

### Beer's Law. Additivity of optical densities

#### (1) The Lambert-Beer law

Consider a beam of monochromatic light passing through a thickness  $l$  of a solution of an absorbing material (Fig. 1) and let  $I_0$  and  $I$  be the respective

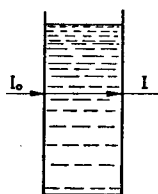


Fig. 1.

intensities of the beam before entering and after leaving the solution. If the concentration of the absorbing material is  $c$ , then according to the Lambert-Beer law

$$\log \frac{I_0}{I} = \epsilon l c.$$

This law states that the proportion of light absorbed does not depend on the incident intensity, and that it varies as the total number of absorbing molecules or ions encountered by the light; *i.e.* that  $l$  and  $c$  play the same role.

(i) *Definitions.* The 'transmittance'  $T$  is defined as the ratio of the two luminous intensities  $T = I/I_0$ . The optical density  $D$  (or extinction  $E$ , or absorbance  $A$ ) is the logarithm of the inverse ratio  $D = \log I_0/I$ . The length  $l$  is always expressed in centimetres.  $\epsilon$  is called the molar extinction coefficient if the concentration is expressed in gram-ions or moles per litre.

NOTE. Beer's law remains valid only if the luminous energy absorbed is converted into thermal energy. Deviations from the law are observed if any fluorescence occurs, or if the solution is colloidal (loss of light by reflection and diffusion).

(ii) *Properties of the extinction coefficient.* According to Beer's law,  $\epsilon$  is independent of the concentration. In the case of solutions, it depends on the dis-

solved material, the wavelength and the temperature, being in principle independent of the solvent.

As an example, the molar extinction coefficient  $\epsilon$  of the permanganate ion is plotted as a function of the wavelength  $\lambda$  in Fig. 2, showing that permanganate possesses an absorption band (region of maximum absorption) at about 500–570  $m\mu$ .

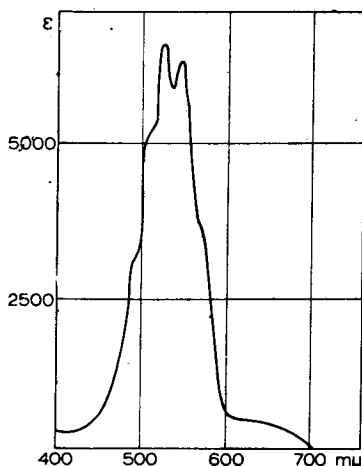


Fig. 2.

The extinction coefficient can vary considerably, the highest values known being in the region of 100,000 (for rhodamine B chloroantimonate).

The shape of absorption curves, such as that illustrated in Fig. 2, depends on the temperature, the absorption bands being as a rule displaced towards longer wavelengths at higher temperatures. The influence of temperature on  $\epsilon$  is therefore particularly marked when the slope  $d\epsilon/d\lambda$  of the curve  $\epsilon = f(\lambda)$  is large, *i.e.* at the edges of the absorption bands.

For example, the extinction coefficient of the *o*-dinitrophenoxide ion, which has an absorption maximum at about 336  $m\mu$ , varies by  $-0.3\%$  per degree at 334  $m\mu$ ,  $+1\%$  per degree at 436  $m\mu$ , and is temperature independent at 366  $m\mu$  (G. KORTÜM, *Z. Phys. Chem.*, 170 (1934) 212).

The variations are generally of this order of magnitude.

## (2) Additivity of optical densities

Consider a monochromatic beam of light passing successively through two different solutions of the same thickness  $l$ , and let  $\epsilon_1$  and  $c_1$ , and  $\epsilon_2$  and  $c_2$ , be their respective extinction coefficients and concentrations (Fig. 3).

The total optical density is then

$$D = \log \frac{I_0}{I_2} = \log \frac{I_0}{I_1} \cdot \frac{I_1}{I_2} = \log \frac{I_0}{I_1} + \log \frac{I_1}{I_2} = D_1 + D_2.$$

This value depends only on the number of absorbing particles encountered and would be the same if the two absorbing compounds were dissolved, in the same concentrations, in a single solution of thickness  $l$  (Fig. 4).

This may, in general, be written:

$$D = \epsilon_1 c_1 l + \epsilon_2 c_2 l + \dots \epsilon_n c_n l.$$

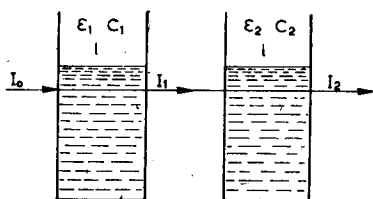


Fig. 3.

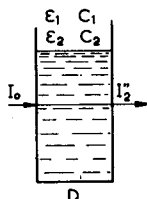


Fig. 4.

This relationship is important being, as will be shown, the basis of most determinations and, in particular, permitting the estimation of absorbing materials in the presence of one another.

**Importance of Beer's law.** The extent to which Beer's law holds true is an important factor, since it makes available a measurable magnitude  $D$  which is proportional to the concentration to be determined. Beer's law need of course only hold true to the extent that the experimental error involved in applying the formula is negligible, *i.e.* the approximation can be of the order of 0.2%, 1%, etc., according to circumstances.

When this law is not obeyed, the calibration of the system prior to measurement is complicated (see p. 51), and mixtures of coloured materials and also the performance of a blank test present problems which are relatively difficult to solve (see p. 63).

It is therefore important to know what are the reasons for failures of Beer's law and to determine the limits of its application.

### (3) Validity of Beer's law

Beer's law is a limiting law which requires ideal conditions both for the beam of light, which must be monochromatic, and for the solution, in which the absence of any action on the absorbing material not due to the beam of light is assumed. We shall consider in turn several different causes of any deviations which may arise.

### (3a) *Refractive index of the solution*

The coefficient  $\epsilon$  depends on the refractive index  $n$  of the solution. According to theory of dispersion it is not  $\epsilon$ , but the function  $\frac{\epsilon n}{(n^2 + 2)^2}$  which is independent of the concentration. Generally  $n$ , and consequently  $\epsilon$ , increase with the concentration of the dissolved material (since  $n > 1$ ).

In the majority of measurements the relative error rarely reaches 0.1% and is therefore negligible if the concentration does not exceed  $10^{-2} M$ . This is no longer the case at higher concentrations and in certain particular cases. *e.g.* eosin in 0.07  $M$  solution gives a deviation of 1.8% at 527  $m\mu$  (G. KORTÜM, *Z. Phys. Chem., B.*, 33 (1936) 243).

### (3b) *Molecular or ionic interactions* *Chemical reactions*

The electronic state of an absorbing molecule or ion may be disturbed by other molecules or ions of the same species which surround it. This disturbance may also be due to molecules of the solvent or of the compounds dissolved in the same solution. These effects are very variable, ranging from simple mutual 'orientation' and 'association' between polar molecules to chemical reactions in the fullest sense.

This explains the (sometimes very slight) variations which can be observed on passing from one solvent to another. For example, the absorption maximum of benzeneazophenol changes from 348 to 351  $m\mu$  and the corresponding extinction coefficient from 26,100 to 26,300 when normal butyl alcohol is used as a solvent instead of methanol (according to W. R. BRODE, *J. Phys. Chem.*, 30 (1926) 56). This interaction is also the cause of the slight variations in  $\epsilon$  which may be observed on addition of a large excess of a nonabsorbing compound.

The interactions between absorbing particles increase with their concentration and consequently lead to a variation of  $\epsilon$  with  $c$ . These interactions can only be determined experimentally. For example, the molar coefficient of the chromate ion  $\text{CrO}_4^{2-}$  in the presence of  $5 \times 10^{-3} M$  sodium hydroxide varies by 0.76% at 436  $m\mu$  when the concentration changes from  $6.8 \times 10^{-4}$  to  $3.7 \times 10^{-2} M$ , and by only 0.02% at 303  $m\mu$  when the concentration changes from  $9.8 \times 10^{-4}$  to  $1.9 \times 10^{-2} M$  although no known chemical reaction takes place (G. KORTÜM, *Z. Phys. Chem., B.*, 33 (1936) 243).

A further example of disturbance due to foreign salts is also given by KORTÜM (*Z. Phys. Chem., B.*, 30 (1935) 317); the molar coefficient of  $10^{-4} M$  dinitrophenoxide ion in a  $10^{-3} M$  solution of potassium hydroxide at 436  $m\mu$  varies by 0.5% when  $10^{-1.3} M$  sodium perchlorate or  $10^{-2.6} M$  lanthanum nitrate is added.

(i) *Chemical equilibria.* In contrast to these small variations, the deviations

caused by the recurrence of chemical reactions are often very important. Thus, the dimerization of methylene blue causes its molar extinction coefficient (at pH 3.4 and 656.5 m $\mu$ ) to change from 38,800 to 16,700 when the concentration is increased from  $2 \times 10^{-6}$  to  $2 \times 10^{-3}$  M (E. RABINOVITCH AND L. F. EPSTEIN, *J. Amer. Chem. Soc.*, 63 (1941) 69).

In this case, the deviation is predictable and can sometimes be reduced by certain operative procedures.

Consider, for example, a complex AB which dissociates according to  $AB \rightleftharpoons A + B$ , with  $\frac{[A][B]}{[AB]} = K$ . Let  $\alpha$  be the degree of dissociation (the fraction of [total AB] dissociated) and  $c_0$  the total concentration. Then:

$$\frac{\alpha^2 c_0}{c_0(1 - \alpha)} = K, \quad \text{or} \quad \frac{\alpha^2}{1 - \alpha} = \frac{K}{c_0}$$

It is thus clear that further dissociation of the complex may be promoted by lowering  $c_0$ . Values of [AB] as a function of the total concentration for the cases  $K = 10^{-4}$  and  $K = 10^{-10}$  are tabulated below to illustrate this point (Table 1).

TABLE 1

$c_0$	[AB] for $K = 10^{-4}$	[AB] for $K = 10^{-10}$
$10^{-1}$	$0.997 \times 10^{-1}$	$0.999 \times 10^{-1}$
$10^{-2}$	$0.905 \times 10^{-2}$	$0.999 \times 10^{-2}$
$10^{-3}$	$0.78 \times 10^{-3}$	$0.997 \times 10^{-3}$
$10^{-4}$	$0.40 \times 10^{-4}$	$0.990 \times 10^{-4}$

The same argument applies to the dissociation of acids.

When the complex is considerably dissociated, Beer's law is *apparently* no longer obeyed.

If  $\alpha$  is to remain less than 1%, it is sufficient that  $K/c_0 \leq 10^{-4}$ , so that the deviation remains negligible, to within 1% or less, as long as  $c \geq 10^4 K$ . In other words, the more stable complexes can be diluted to a greater extent, without disturbances being observed (see G. CHARLOT AND R. GAUGUIN, *Les methodes d'analyse des reactions en solution*, Masson, Paris, 1951).

If the complex is not too unstable,  $\alpha$  can still be kept below 1%, in spite of dilution, by adding a large excess of complexing ions.

If the complex is very unstable, the excess concentration of the complexing agent must be kept constant during dilution.

Other expedients may be used in particular cases. For example, let us consider the determination of the concentration of a compound such as bromophenol

blue R, which takes part in the equilibrium  $R \rightleftharpoons R^- + H^+$ , where R and  $R^-$  are of different colour. The optical density of this system is given by:

$$D = \epsilon_R l c(1 - \alpha) + \epsilon_{R^-} \cdot l \alpha c = l c [\epsilon_R(1 - \alpha) + \epsilon_{R^-} \cdot \alpha],$$

where  $c$  is the total concentration of bromophenol blue.  $D$  is proportional to  $c$  if  $\alpha$  is constant, or if  $\epsilon_R = \epsilon_{R^-}$ . The first condition is realized in a medium buffered with respect to the pH; the second is achieved by carrying out the measurements at the wavelength of the isobestic point ( $\epsilon_R = \epsilon_{R^-}$ ).

NOTE. In the case of chemical side reactions, additional deviations from Beer's law are caused by the foreign salts present and by the temperature, apart from their action mentioned above. Thus the dissociation of complexes is increased at higher temperatures and is affected by changes in the ionic strength  $I$ , consequent upon the addition of foreign salts to the solution.

For example, in the case of the ferrithiocyanate equilibrium:

$$\frac{c_{Fe^{3+}} \cdot c_{SCN^-}}{c_{FeSCN^{2+}}} = K \frac{f_{FeSCN^{2+}}}{f_{Fe^{3+}} \cdot f_{SCN^-}} = K',$$

where  $f$  is the activity coefficient. To a first approximation,  $K'$  is increased by a factor of 5 when the ionic strength  $I$  changes from  $10^{-2}$  to  $10^{-1}$ . Consequently, if an excess of  $SCN^-$  is added, such that  $c_{SCN^-} = K'$  for  $I = 10^{-2}$ , for  $I = 10^{-1}$ , we have  $c_{SCN^-} = K'/5$ ; thus  $\alpha$  changes from  $1/2$  to  $5/6$ . If we had taken  $c_{SCN^-} = 100 K'$  for  $I = 10^{-2}$ ,  $\alpha$  would have changed from 0.01 to 0.05. The effect of the ionic strength becomes negligible in the case of very stable complexes.

### (3c) Deviations due to the polychromaticity of the light used

In principle, Beer's law is only valid for ideally monochromatic light. In practice, this is never available.

Consider two beams with different wavelengths  $\lambda$  and  $\lambda'$  and intensities  $I_0$  and  $I'_0$ . We have:

$$\log \frac{I_0}{I} = \epsilon_\lambda l c \text{ and } \log \frac{I'_0}{I'} = \epsilon_{\lambda'} l c.$$

If Beer's law were obeyed for all of the light used, we should have:

$$\log \frac{I_0 + I'_0}{I + I'} = \epsilon l c,$$

which obviously cannot be deduced from the previous relation which, on the contrary, gives:

$$\log I_0 + \log I'_0 - (\log I + \log I') = (\epsilon_\lambda + \epsilon_{\lambda'}) l c.$$



Measuring devices (eye or photoelectric cell) are sensitive to  $mI + nI'$  and not to  $\log I + \log I'$ , and their readings will therefore no longer be proportional to  $c$ .

NOTE. It is only in the case where  $\epsilon_\lambda = \epsilon_{\lambda'}$  that we can write:

$$\frac{I_0}{I} = \frac{I_0}{I'} = \frac{I_0 + I'_0}{I + I'} \text{ and } \log \frac{I_0 + I'_0}{I + I'} = \epsilon_\lambda lc.$$

More precisely, let us suppose that the total intensity  $I_0 + I'_0$  is kept constant. If a greater proportion of the less absorbed radiation is present, the total emergent intensity increases and the apparent optical density is decreased.

It should also be noted that the emergent light is richer in the less absorbed radiations than the incident light. If then a second solution identical with the first is placed in the path of the beam emerging from the latter, by applying the results obtained with a single solution, we see that the second solution is illuminated with a light richer in the less absorbed radiation and that, consequently, its apparent optical density is less than that of the first solution:  $D_2 < D_1$ . For each monochromatic part of the beam, only the number of absorbing particles encountered comes into consideration, *i.e.* the product  $lc$ . As the same argument obviously applies to the superposition of different beams, it may be concluded that when it is no longer  $l$  but  $c$  which is multiplied by 2, an optical density equal to less than twice the initial value is obtained. A more detailed study would show that the apparent extinction coefficient lies between the extreme values of those of the different incident beams and that, when  $c$  increases, it tends towards the minimum of these coefficients. Furthermore, this tendency is the more rapid the richer is the incident light in the less absorbed radiation.

EXAMPLE. Two identical cells 1 cm thick were filled with 0.1 *N* dichromate. Using a Wratten No. 38 filter (light blue, with a transmission maximum at 460  $m\mu$  and a wide transmission band), the optical density of each of them was established as 0.284. When the two cells were placed simultaneously in the path of the light beam, the optical density of the combination was found to be 0.381 instead of 0.568. According to this final result, the apparent optical density of the second cell, is 0.097 instead of 0.284.

In practice, the range of wavelengths used is never zero and  $\epsilon_\lambda$  is not generally constant. The ideal conditions are approached by reducing the range of wavelengths or by selecting it so that it straddles a maximum (or a minimum) of the  $\epsilon = f(\lambda)$  curve of the material under consideration. Under these conditions, the variations of  $\epsilon_\lambda$  for the beam used are reduced and Beer's law is obeyed, to a certain degree of approximation, over a wider range of concentrations.

EXAMPLE. A permanganate solution has two absorption maxima, at 524 and