SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 7, Nº 8, 1999

HEIGHT MEASUREMENTS OF THE SPECTRUM AS AN ALTERNATIVE TO CONVENTIONAL SPECTROPHOTOMETRIC ANALYSIS OF A $KMnO_4$ - $K_2Cr_2O_7$ MIXTURE

Carmem D. Cardoso, Martha B. Adaime and Nádia S. Viaro
Departamento de Química - Universidade Federal de Santa Maria
Campus Camobi - Km 09 - CEP: 97.119-900 - Santa Maria - RS - Brasil

ABSTRACT

Quantitative spectrophotometric analysis is generally carried out plotting absorbance against concentration, for some concentration range, in accordance with Lambert, Bourger and Bee law. In this work, height measurement of the spectrum was used to analyse $KMnO_4$ and $K_2Cr_2O_7$ mixtures in two different known concentrations. The experiments were relatively simple to carry out, requiring only standard solutions of $KMnO_4$, $K_2Cr_2O_7$, sample mixtures of the two components, a visible light spectrophotometer, recorder, ruler and pencil. Comparison of the two methods showed that the height measurement method is more reliable and versatile as it has no requirement for the calculation of molar absorptivity, shows less relative error than the conventional method.

RESUMO

Análises espectrofotométricas quantitativas geralmente são efetuadas relacionando absorbância e concentração, segundo a lei de Lambert, Bourger e Beer. Neste trabalho, usa-se medidas da altura de espectros para analisar misturas de concentrações conhecidas de $KMnO_4$ e $K_2Cr_2O_7$. Os experimentos são relativamente simples de serem desenvolvidos, necessitando somente soluções padrões de $KMnO_4$, $K_2Cr_2O_7$, misturas dos dois componentes, fonte de luz visível para o espectrofotômetro, registrador, borracha e lápis. Comparando-se os dois métodos, observou-se que o método de medida de altura é mais seguro e versátil, pois não necesstita de cálculo de absortividade molar, mostrando menor erro relativo do que o método convencional.

Keywords
Height measurements, spectrophotometric analysis, $KMnO_4$-$K_2Cr_2O_7$ mixture, quantification

DOI: 10.48141/SBJCHEM.v7.n8.1999.87_1999.pdf

INTRODUCTION

During the development of a quantitative method fot the determination of an unknown concentration of a species using absorption spectrophotometry in the ultraviolet and visible regions, the first step is the choice of the maximun absorption wavelength where the measurements are made. At this wavelength the absorbance of the solution has a linear relation to its concentration within a defined concentration range, following the Lambert, Bourger and Beer law[1]. This is the classic method used in quantitative analysis.

To determine two compounds simultaneously by molecular absorption spectrophotometry, these determinations can be made based on absorption measurements at two selected wavelengths, from which a pair of simultaneous equations are obtained, taking into account that the absorbance is an additive property[2]. It is necessary also to measure (or otherwise obtain) the molar absorptivity of each pure compound at the two predetermined wavelengths. When there are more than two compounds in the mixture with superposition of absorption spectrum, more simultaneous equations are required and, consequently software is necessary to resolve them[3].

Another quantitative method for mixtures is by using graphs to solve the simultaneous equations. For mixtures of three compounds, the solution to the problem is obtained by a triangular diagram for mixtures of four compounds a tridimensional diagram - a tetrahedron is used[4].

As an alternative method, when mixtures are involved with overlapping spectra, many wavelengths must be determined so that linear diagrams can be made from which the concentrations can be determined. This method can be applied to mixtures of two or more components[4].

The measurement of the area of the spectrum and the absorbance band height at different points of the spectrum has also been used sucessfully[5].

The purpose of the present work was to show the effectiveness of the spectrum height measurement for the simultaneous quantitative analysis of a mixture of $KMnO_4$ and $K_2Cr_2O_7$ using the spectrophotometric method.

EXPERIMENTAL PROCEDURE

All the reagents were of analytical grade. Stock solutions of 0.01 mol L^{-1} $KMnO_4$ and 0.02 mol L^{-1} $K_2Cr_2O_7$ were prepared in previously boiled and cooled deionized water containing 5 mol L^{-1} H_2SO_4. The concentration of the $KMnO_4$ solution was determined titrimetically against $H_2C_2O_4$ 0.01 mol L^{-1} [6].

Then, 13 standard solutions of the individual components, were prepared in 50 mL volumetric flasks completing the volumes with deionized water.

Sample mixtures with known concentrations were also prepared as follows: A - 2 mL of 0.01 mol L^{-1} $KMnO_4$ solution, 5 mL of 0.02 mol L^{-1} $K_2Cr_2O_7$ solution and 5 mL of 5 mol L^{-1} H_2SO_4 solution; B - 1 mL of 0.01 mol L^{-1} $KMnO_4$ solution, 2 mL of 0.02 mol L^{-1} $K_2Cr_2O_7$ solution and 5 mL of 5 mol L^{-1} H_2SO_4 solution.

The absorption spectra of each standard solution was measured between 400 to 600 nm on a Perkin Elmer 124 spectrophotometer and recorded on a Perkin Elmer 56 recorder. A cell of 1 cm was used while the attenuation was 10 mV and the chart speed was 20 mm.min^{-1}.

Height measurements' were made at 1.1 cm (λ=560 nm) from the origin for the $KMnO_4$ spectra (h_1) and at 5.3 cm (λ=449 nm) of the origin from the $K_2Cr_2O_7$ spectra (h_3).

Table I lists the data used to make the plot of the $KMnO_4$ standard solutions while Table II lists the data used to make the plot of the $K_2Cr_2O_7$ standard solutions.

These heights were plotted against the respectives concentrations as shown in Figures 3 and 4.

The spectra of mixture A and B were also recorded from 400 to 600 nm of wavelength. Height measurements were made at the same positions as for the individual solutions.

RESULTS AND DISCUSSION

From height readings' at 1.1 cm from the origin of mixtures' spectra, according Figures 1 and 2, the $KMnO_4$ concentration can be determined directly from the linear plot of h_1 (height) x C (concentration), Figure 3.In this situation, there was no interference from the $K_2Cr_2O_7$ solution, giving a $KMnO_4$ concentration of 4.0 x 10^{-4} mol L^{-1} for mixture A and, for mixture B, a concentration of 2.0 x 10^{-4} mol L^{-1}.

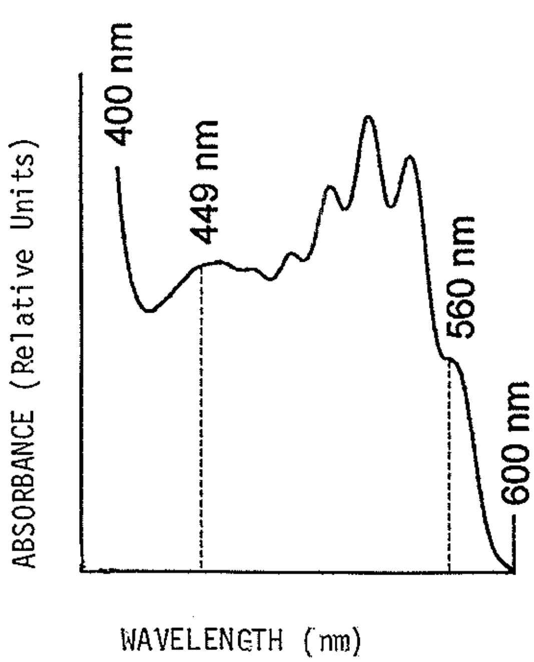

Figure 1. Absorption spectrum of the mixture A.

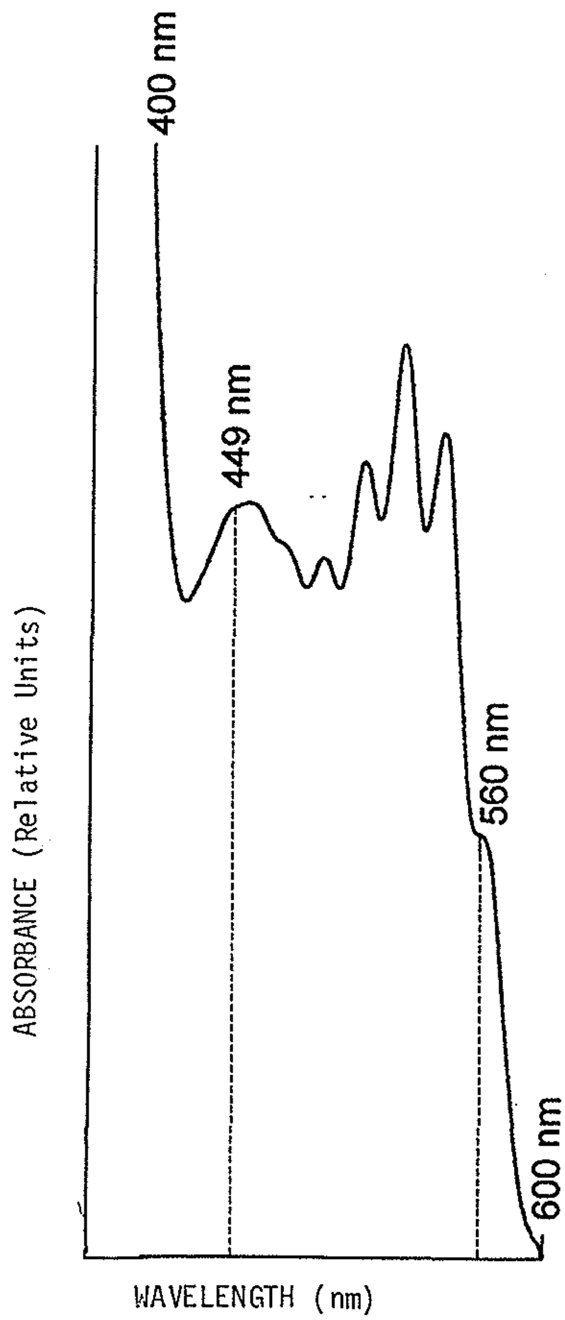

Figure 2. Absorption spectrum of the mixture B.

$KMnO_4$ standard solutions were prepared on the obtained concentrations from the mixtures and they were used to make the absorption spectra. The heights were measured on the same wavelength that was measured h_1. For mixture A, h_1A it was of 12.5 cm and h_2A it was of 0.8 cm and for mixture B, h_1B it was of 5.1 cm and h_2B of 0.35 cm.

Table I. Spectral height data of $KMnO_4$ standard solutions measured at 560 nm.

Volume $KMnO_4$ 0.01mol L^{-1} (mL)	Volume H_2SO_4 5 mol L^{-1} (mL)	Concentration (x 10^4 mol L^{-1})	Concentration (mg L^{-1})	h_1(height) (cm)
0.4	5	0.8	12.64	1.30
0.7	5	1.4	22.12	2.30
1.0	5	2.0	31.60	3.15
1.3	5	2.6	41.08	3.80
1.6	5	3.2	50.56	5.25
1.9	5	3.8	60.04	6.00
2.2	5	4.4	69.52	7.40
2.5	5	5.0	79.00	8.10
2.8	5	5.6	88.48	9.50
3.1	5	6.2	97.96	10.75
3.4	5	6.8	107.44	12.15
3.7	5	7.4	116.92	13.15
4.0	5	8.0	126.40	14.30

Table II. Spectral height data of $K_2Cr_2O_7$ standard solutions measured at 449 nm.

Volume $KMnO_4$ 0.02 mol L^{-1} (mL)	Volume H_2SO_4 5 mol L^{-1} (mL)	Concentration (x10^3 mol L^{-1})	Concentration (mg L^{-1})	h_3(height) (cm)
1.0	5	0.4	117.6	2.8
1.5	5	0.6	176.4	4.0
2.0	5	0.8	235.2	5.5
2.5	5	1.0	294.0	6.3
3.0	5	1.2	352.8	8.0
3.5	5	1.4	411.6	9.0
4.0	5	1.6	470.4	9.0
4.5	5	1.8	592.2	11.5
5.0	5	2.0	588.0	12.5
5.5	5	2.2	646.8	13.8
6.0	5	2.4	705.6	15.5
6.5	5	2.6	764.4	16.2
7.0	5	2.8	823.2	17.6

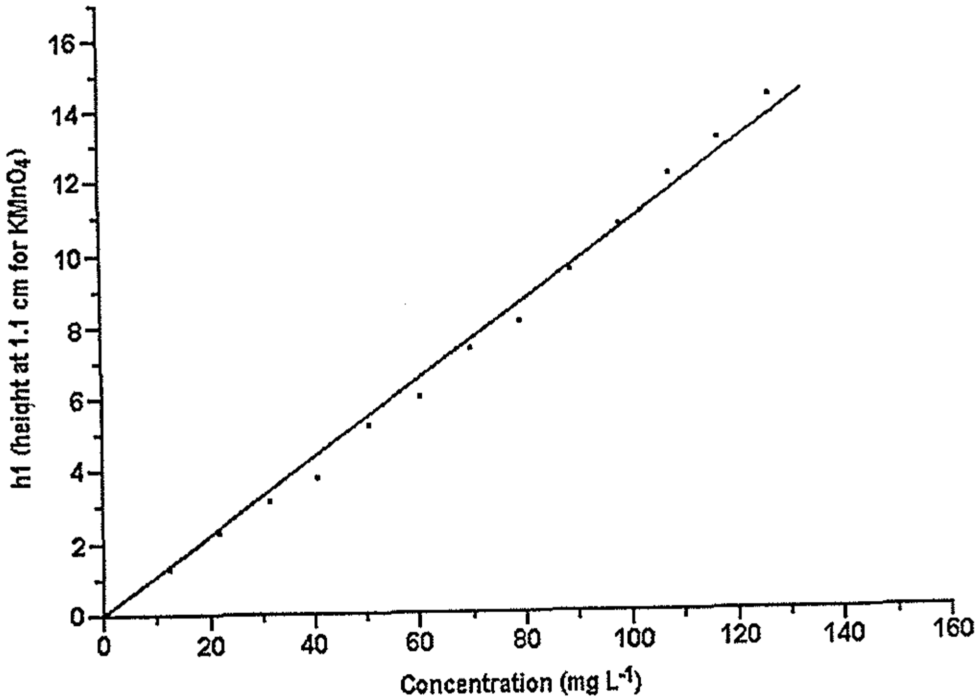

Figure 3. Plot of height (h_1) versus the concentration of $KMnO_4$ at 1.1 cm. Data from Table I.

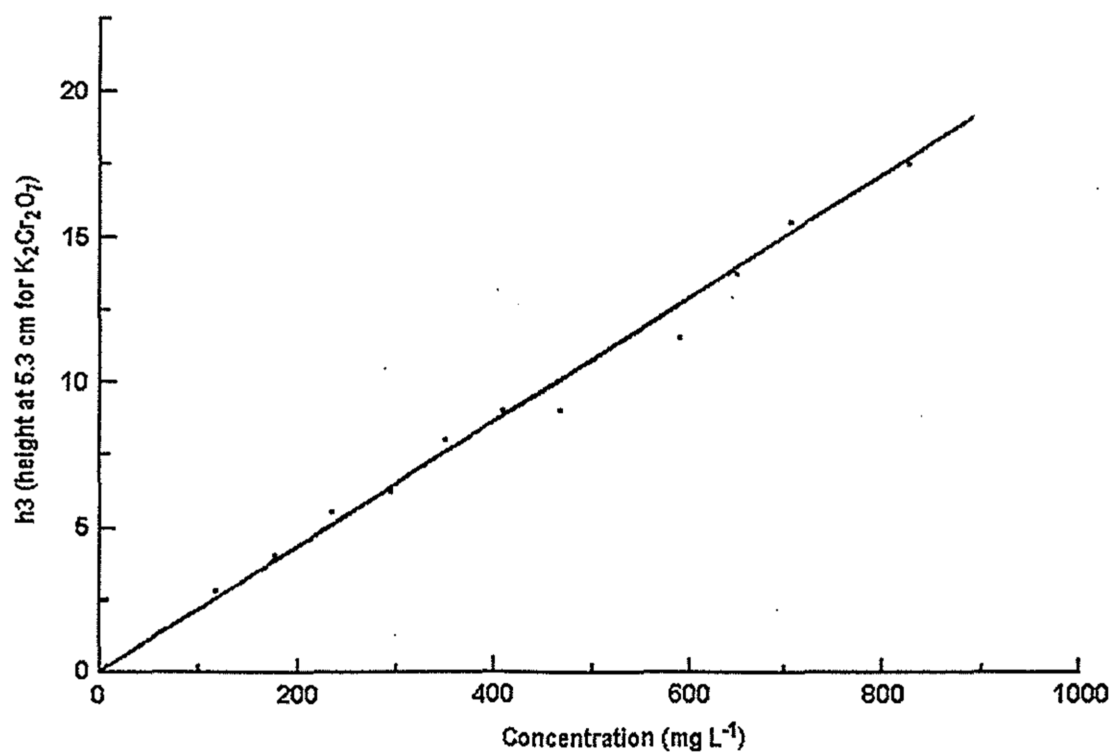

Figure 4. Plot of height (h_3) versus the concentration of $K_2Cr_2O_7$ at 5.3 cm. Data from Table II.

Table III. Results for the two-component mixtures by the conventional and the alternative methods.

Mixtures		Calculated concentration (x 10^4 mol.L^{-1})	Method 1 (x10^4 mol.L^{-1})	Relative Error (%)	Method 2 (x 10^4 mol.L^{-1})	Relative Error (%)
A	$KMnO_4$	4.0	4.0	0.0	5.0	+ 25.0
	$K_2Cr_2O_7$	20.0	18.0	- 10.0	27.0	+ 35.0
B	$KMnO_4$	2.0	2.0	0.0	2.8	+ 40.0
	$K_2Cr_2O_7$	8.0	7.3	- 8.8	10.0	+ 25.0

Method 1 - Alternative method (Height Measurement)
Method 2 - Conventional method using simultaneous equations

Considering the total height (h_t) measured at 5.3 cm for the mixtures as the sums of the contributions from $KMnO_4$ and $K_2Cr_2O_7$:

$$h_t = h_2 + h_3 \qquad (1)$$

Then, from: h_3=h_t - h_2, the values of h_3 were calculed (mixture A, h_3=11.7 cm and mixture B, h_3=4,75 cm). From Figure 4, the determined $K_2Cr_2O_7$ concentrations' for mixtures A and B were 1,8 x 10^{-3} mol L^{-1} and 7.3 x 10^{-4} mol L^{-1}, respectivelly.

Table III gives comparative data for the conventional and this alternative method.

The conventional method uses simultaneous equations, so as many equations as the number of components in the mixture are necessary, requiring values of molar absorptivity as well as absorbances and known concentrations. The relation height versus with this concentration brings the reality nearer than the relation absorbance versus concentration. With this alternative method is not necessary to calculate molar absorptivity and the relative error is smaller compared to the conventional method.

ACKNOWLEDGMENT

The authors would like to thank FIPE (Brazil) for financial support of this work and Dr. Carol Collins for useful suggestions.

REFERENCES

1. J. Robinson,. W.*Undergraduate Instrumental Analysis*; 4th ed.; Dekker Inc: New York,,USA,1987, p 54.

2. H. H. Willard; L. L. Merrit, Jr.; J. A. Dean and F. A. Settle, Jr., *Instrumental Methods of Analysis*, 6th ed.; Wadsworth Publishing Co; Belmont, California. USA, 1981, Vol. 1, p 77.

3. I. Giolito, *Medidas Fotométricas*, Faculdade de Farmácia e Bioquímica da USP, São Paulo, Brasil,1968, p 51.

4. A. C. Kenneth, and J. E. Chukwuenweniwe, *Analytical Chemistry*, 51(8), 1262-1266, (1979).

5. C. D. Cardoso; I. Ramires; I. Santos; M. B. Adaime and N. S. Viaro, *Química Nova*, 14(4), 49, (1991).

6. O. A. Ohlweiler, *Química Analitica Quantitativa*, Livros Técnicos e Científicos Editora , Rio de Janeiro, Brasil, 1976, Vol. 2, p. 571.