AN EMPIRIC PROCEDURE FOR MODIFIED UTILIZATION OF DEER-LAMBERT LAW FOR THE SPECTROMETRIC ANALYSIS OF SIMPLE SOLUTIONS

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ABSTRACT- The publication gives an alternative empiric procedure for application of Beer-Lambert law. It rests on determining the area under the peak of maximum absorbance of analyte (A) in solution instead of the absorbance at maximum wavelength as a function of concentration. This empiric procedure gives straight line relations between the area and concentration. Calculation of molar absorptivity, ε, for taking the absorbance and area under the peak of maximum absorbance percentage and relative errors prove that the proposed procedure is more precise and reliable. The study has been made on solutions of cerium and some transition elements in addition to complex with KI or Co 1,2 hls (beta-aminethoxy) ethane, N, N', N'', N''' sodium sulfonate trisacetic acid. A proposal is put forward to modify the new generations of spectrometers by adding electronic integrators and computer possibilities to obtain more precise and reliable results.

INTRODUCTION

Spectrometric procedures of analysis have been developed for many determinations of interest as to environmental analysis. Deviations from Beer-Lambert law may be smallest when the slit entrance is narrow as possible and when the Intensity of the incident beam coincides the absorption of the analyte in the sample [1-5].
The development of a procedure to widen the applicability of Beer-Lambert law is appreciated. The idea was deduced from the developments that happened in chromatographs, multi-channel analysers and other instruments in which calculations based on the height of the peak is replaced by the area under it.

EXPERIMENTAL

Solutions were prepared from analytical grade reagents and distilled water. The pH of the prepared solutions and reference samples was adjusted at 5.5 by sodium hydroxide or hydrochloric acid solution using the pH meter 7018 Electronic Instrument Limited. The absorbance measurements of the prepared solutions were carried out at laboratory temperature 25 °C using CE 599 Universal Automatic Scanning Spectrophotometer, (Cecil Instruments Limited, England).

The stock solution of 1.2 % (beta-aminooxy) ethane N, N, N’ , N”- tetraamine (ASTA), which can be noted as NaH₂Y, having the molarity 7 x 10⁻³ M was standardized against standard copper sulphate solution using mercuric solution as indicator and ammonium chloride as buffer solution at pH 8 according to the method of Schwarzenbach [6]. Standardization of other solutions was made according to published methods [6,7].

The spectra of prepared solutions at different concentrations were scanned. The absorbance values at λ_max determined. The areas under the obtained curves were determined by 13201 zero-setting Polar planimeter. The standard errors of ε at the working conditions were determined.

RESULTS AND DISCUSSION

Figures (1-5) show the absorbance of variable concentrations of NaCl₂, \( \text{Na}^+ \), \( \text{SnCl}_2 \), \( \text{Cu}^+ \), and \( \text{Co} (\text{SO}_4)_2 \) solutions at pH 5.5. Figures (6-10) show the application of Beer's law and the area under the peak to determine the concentration of the analyte in solutions. It is clear that both approaches give straight lines. This indicates that taking variations of areas as a function of concentration is possible.

A comparison between the degree of accuracy for taking absorbance or area under the peak as a function of concentration has been made. The values of absorbance, standard deviations \( \sigma_n \) and \( \sigma_{n-1} \) and percentage error in the calculation of molar absorptivity are compared.

Table (1) shows the average molar absorptivities that are calculated when taking absorbance (Beer-Lambert law) or area ε as a function of concentration at the prevailing conditions. The determined values of ε are reasonable and close to what are published [6]. The calculations show that the percentage error of the obtained molar absorptivities \( \epsilon_n \% \) and \( \epsilon_{n-1} \% \) in case of taking area is generally less than those in case of taking absorbance. The table demonstrates also, that the molar absorptivity ε, in case of taking area, is larger higher than that of taking absorbance. Therefore, taking the area and the corresponding molar absorptivity enable us to determine up to 20-100 times less of concentration value than if we take absorbance. Moreover, taking the area instead of absorbance at λ_max may avoid the shiftings of maximum wavelength with dilution process [2-4] and as a result the range of applicability of Beer-Lambert law can be widened.

It can be concluded that better application of Beer-Lambert law can be obtained if the value of areas under the peaks are taken as a measure of the
concentration instead of absorbance. Therefore addition of electronic integrators and computer possibilities of addition and subtraction of areas and others, as optional parts, will be important for the new generations of spectrometers to able users to determine areas under the peaks as well as absorbance at the maximum real wavelength simply and accurately at the same time.

REFERENCES:


Legends of Figures:

Figure (1): Absorbance spectra of NiCl₂ at pH 5.5 of variable concentrations, where:
(1) 5 x 10⁻², (2) 6 x 10⁻², (3) 7 x 10⁻² and (4) 8 x 10⁻² M solution of NiCl₂.

Figure (2): Absorbance spectra, at pH 5.5, of NiY of variable concentrations, where:
(1) 1 x 10⁻², (2) 2 x 10⁻², (3) 3 x 10⁻² and (4) 4 x 10⁻² M solution of NiY solution.

Figure (3): Absorbance spectra of CoCl₂ at pH 5.5 of variable concentrations, where:
(1) 1 x 10⁻², (2) 2 x 10⁻², (3) 4 x 10⁻² and (4) 6 x 10⁻² M CoCl₂ solution.
Figure (4): Absorbance spectra of CeO₄²⁻ at pH 5.5 of variable concentrations, where:
(1) 0.5 x 10⁻², (2) 1 x 10⁻², (3) 1.5 x 10⁻² and (4) 2 x 10⁻² M solution of CeO₄²⁻.

Figure (5): Absorbance spectra of Ce₂(SO₄)₃ at pH 5.5 of variable concentrations
where: (1) 0.7 x 10⁻⁴, (2) 1.4 x 10⁻⁴, (3) 2.1 x 10⁻⁴ and (4) 2.8 x 10⁻⁴ M solution of Ce₂(SO₄)₃.

For Figures (6-10):
Application of Beer's Law and the recommended calculation of the area
under the peaks:

Fig. (6) for NiCl₂, Fig. (7) for Ni²⁺
Fig. (8) for CoCl₂, Fig. (9) for Co²⁺
and Fig (10) for Ce₂(SO₄)₃

Boer's Law viz; the relation between absorbance and concentration.

Table (1): Comparison between molar absorptivities
Calculated by the two approaches, viz: Beer-Lambert law and area under the peak.

<table>
<thead>
<tr>
<th>Type of analyte</th>
<th>molar absorptivity (ε) if absorbance A is taken and its statistics</th>
<th>molar absorptivity (ε) if the area under is taken and its statistics the peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCl₂</td>
<td>ε = 5.34, δ̅₂ = 0.041, δ̅₂⁻ = 0.047, δ̅₂⁻ / δ̅₂ = 0.76 / 0.88, δ̅₂⁻² / δ̅₂² = 2.11 / 1.83, δ̅₂⁻² / δ̅₂² = 2.11</td>
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<tr>
<td>Ni²⁺</td>
<td>ε = 12.65, δ̅₂ = 0.41, δ̅₂⁻ = 0.047, δ̅₂⁻ / δ̅₂ = 3.24 / 3.72, δ̅₂⁻² / δ̅₂² = 2.89 / 2.89, δ̅₂⁻² / δ̅₂² = 1.29</td>
<td></td>
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<tr>
<td>CoCl₂</td>
<td>ε = 7.36, δ̅₂ = 2.39, δ̅₂⁻ = 2.76, δ̅₂⁻ / δ̅₂ = 32.5 / 37.5, δ̅₂⁻² / δ̅₂² = 6.32 / 9.60, δ̅₂⁻² / δ̅₂² = 1.29</td>
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<tr>
<td>Co²⁺</td>
<td>ε = 23.25, δ̅₂ = 1.92, δ̅₂⁻ = 2.22, δ̅₂⁻ / δ̅₂ = 8.26 / 9.55, δ̅₂⁻² / δ̅₂² = 6.88 / 9.84, δ̅₂⁻² / δ̅₂² = 0.84</td>
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<tr>
<td>Ce₂(SO₄)₃</td>
<td>4793.41, 719.43, 904.35, 15.01 / 16.78, 4099.53, 2852.11, 9226.11, 2.92 / 2.26</td>
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