An Empiric Procedure for Modified Utilization of Beer-Lambert Law for the Spectrometric Analysis of Simple Solutions.

Mohamed El-Dessouky
Associate Professor., Department of Chemical Engineering., Military Technical College Cairo., Egypt.

Mahmoud El-komy
Department of Physics and Mathematical Sci., Faculty of Engineering (Shoubra)., Zagazig University (Benha Branch).

Ibrahim Rashed
Mathematics and Engineering Physics Department., Faculty of Engineering., El-Mansoura University., Mansoura., Egypt.

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

By

Assoc. Prof. Dr. Eng.
Mohamed M. El-Dessouky

Dept . of Chem. Engg Military Technical
College, Cairo, Egypt

Assoc. Prof. Dr
Mahmoud A. El-Komy

Dept of Phys. and Math. Sci.,
Faculty of Engg (Shoubra), Zagazig
University (Benha Branch)

Prof. Dr. Eng.
Ibrahim G. Rashed

Dept. of Phys., Faculty of Engg, Mansoura Univ.

طريقة تجريبية لتطوير تطبيق قانون ــ لابيرتاا تقدير الطيفى للمحاليل االبسيطة

يتناول البحث طريقة تجريبية لاستخدام قانون بيرــ لابرت وبطاخصرفى تعيين المساحة تحت الانحنى
الناتج من أطياف محاليل قياسية عند تركيزات مختلفة بدلا من الامتصاصة وهذه االطريقة التجريبيـــة
أعطت علاقات خطية بين االمساحات والتركيزات وتمت هذه االدراسة على بعض محاليل العناصر الانتقالية
ومتراكباتها مع ١ و٢ ثنائي (بيتا أمينوايثوكسى) ايثان من ون ونَوَنَ سافونات الصوديوم الثلاثى
حمض الخليك عليه قيم أسرهيد روجينى محددة ٠

وبمقارنة نتائج استخدام الساحات وكذاك الامتصاصة مع اختلاف االتركيزات وبحسا تالامتصاصيـــة
الجزئية وجد أن االطريقة التجريبية المقترحة تعطى نتائج اكثر دقة وأوسع مجالا فى استخدام قانـــون
بير ــ لابرت وتعطى فرصة أكبر لتعيين التركيزات المتاحة فى الاصغر ٠

ويخام البحث الى اقتراح اضافة متكاملات الكترونية للأجيال المستقبلة من أجهزة قياس الطيف فـــى
مجال الاشعة المرئية وفوق البنفسجية لتعيين المساحة تحت الانحنى لأقصى الامتصاصية الكترونيـــا
االحصوا على نتائج أفضل تمشيا مع نفس االتطور الذى حدث لأجهزة الكروماتوجراف وأجهزة التحايـــل
الاشعاعى المتعددة القنوات٠

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 (s) 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 Ni or Co 1,2 bis (beta-aminoethoxy) ethane, N, N, N⁻, N⁻, sodium sulfonate triacetic 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 bidistilled 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 earried out at laboratory temperature 25 °C using CE 599 Universal Automatic Scanning Spectrometer, (Cecil Instruments Limited, England).

The stock solution of 1,2 bis (beta-aminoethoxy) ethane N, N, N'', N''', Sodium sulfonate triacetic acid (ASTA), which can be noted as NaH_3Y, having the molarity 7×10^{-3} M was standardized against standard copper sulphate solution using murexide as indicator and ammonium chloride as buffer solution at pH 8 accor-ding 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} were determined. The areas under the obtained curves were determined by 13201 zero-setting Polar Plani meter. The standard errors of ϵ at the working conditions were determined.

RESULTS AND DISCUSSION

Figures (1-5) show the absorbance of variable concentrations of $NiCl_2$, NiY^{--}, $CoCl_2$, CoY^{--}, and $Ce(SO_4)_2$ 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 analytes in solutions. It is clear that both approaches give straight lines. This indiuates 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, tandard deviations σ_n and σ_{n-1} and percentage error in calculation of molar absorptivity are compared.

Table (1) shows the avarage molar absorptivities that are ealculated when taking absorbance (Beer-Lambert law) or area ϵ^- as a function of concentration at the prevaling 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 $\frac{\sigma_n}{\epsilon}$ % and $\frac{\sigma_{n-1}}{\epsilon}$ % 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 larglx 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 obsorbanee at λ_{max} may avoide the migrations of maximum wavelength with dilution process [9-13], and as a result the range of applicability of Beer-Lambert law can be widended.

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 substraction 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.

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Legends of Figures:

Figure (1) : Absorbance spectra of $NiCl_2$ at pH 5.5 of. variable concentrations, where: (1) 5×10^{-2}, (2) 6×10^{-2}, (3) 7×10^{-2} and (4) 8×10^{-2} M solution of $NiCl_2$

Figure (2) : Absorbance spectra, at pH 5.5, of NiY of variable concentrations, where: (1) 1×10^{-2}, (2) 2×10^{-2}, (3) 3×10^{-2} and (4) 4×10^{-2} M solution of NiY solution.

Figure (3) : Absorbance spectra of $CoCl_2$, at pH 5.5, of variable concentrations, where: (1) 1×10^{-2}, (2) 2×10^{-2}, (3) 4×10^{-2} and (4) 6×10^{-2} M $CoCl_2$ solution.

Figure (4) : Absorbance spectra of CoY, at pH 5.5 of variable   concentrations, where: (1) 0.5×10^{-2}, (2) 1×10^{-2}, (3) 1.5×10^{-2} and (4) 2×10^{-2} M solution of CoY.

Figure (5) : Absorbance spectra of $Ce SO_4)_2$, at PH 5.5 of variable concentrations where: (1) 0.7×10^{-4}, (2) 1.4×10^{-4}, (3) 2.1×10^{-4} and (4) 2.8×10^{-2} M solution of $Ce (SO_4)_2$

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

Fig. (6) for $NiCl_2$,   Fig. (7) for NiY^{--}

Fig. (8) for $CoCl_2$,   Fig. (9) for CoY^{--}

and Fig (10) for $Ce (SO_4)_2$
�‌◻ Beer's Law viz; the relation between absorbance and concentration.

● The recommended theorem,viz: the relation between area and concentration.

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

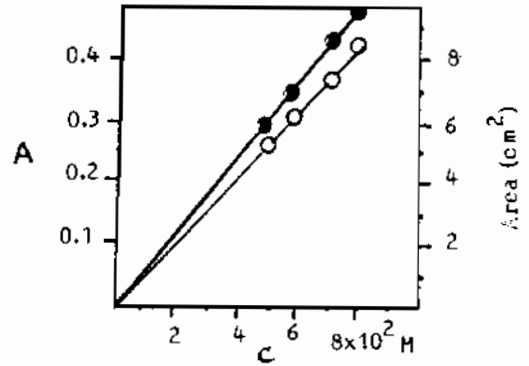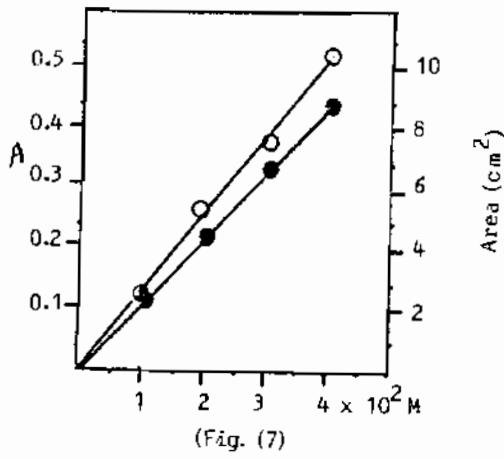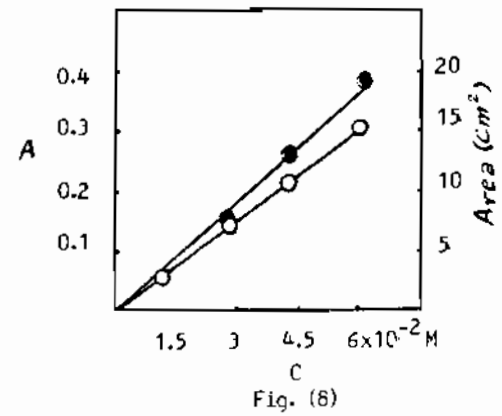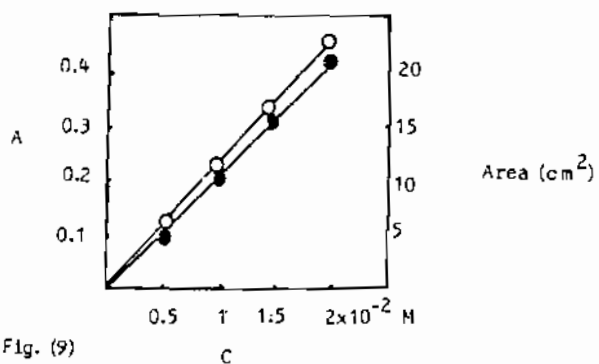| Type of analyte	molar absorptivity (ϵ) if absorbance A is taken and its statistics					molar absorptivity ($\bar{\epsilon}$) if the area under is taken and its statistics the peak				
	ϵ	σ_n	σ_{n-1}	$\frac{\sigma_n}{\epsilon}$ %	$\frac{\sigma_{n-1}}{\epsilon}$ %	$\bar{\epsilon}$	σ_n^-	$\sigma_{n-1}^=$	$\frac{\sigma_n}{\bar{\epsilon}}$	$\frac{\sigma_{n-1}}{\bar{\epsilon}}$ %
$NiCl_2$	5.34	0.041	0.047	0.76	0.88	123.6	1.83	2.11	1.83	2.11
NiY^{--}	12.65	0.41	0.047	3.24	3.72	223.53	2.51	2.89	1.12	1.29
$CoCl_2$	7.36	2.39	2.76	32.5	37.5	342.3	28.52	32.91	8.32	9.60
CoY^{--}	23.25	1.92	2.22	8.26	9.55	1058.25	7.69	8.88	0.73	0.84
$Ce (SO_4)_2$	4793.41	719.43	804.35	15.01	16.78	409023	2852.11	9226.11	2.02	2.26
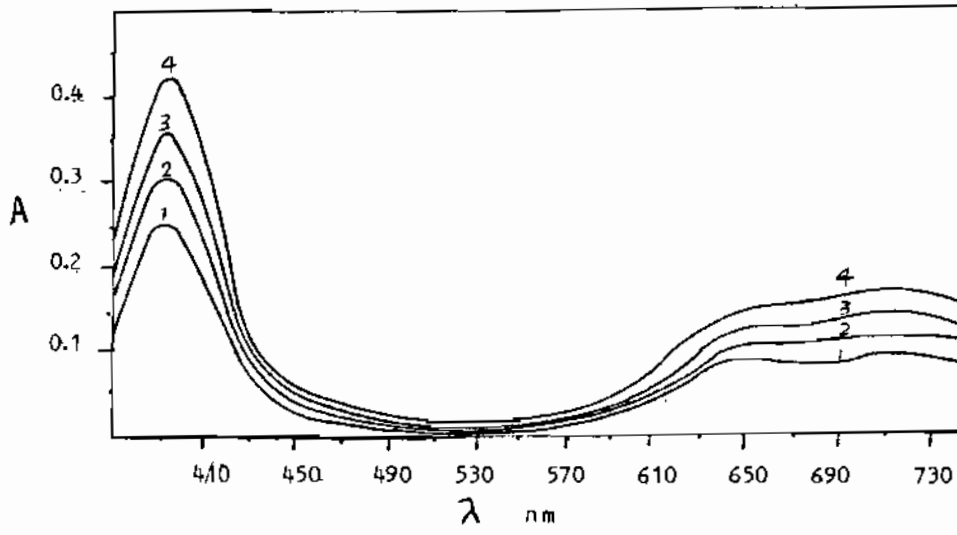
Fig. (1)
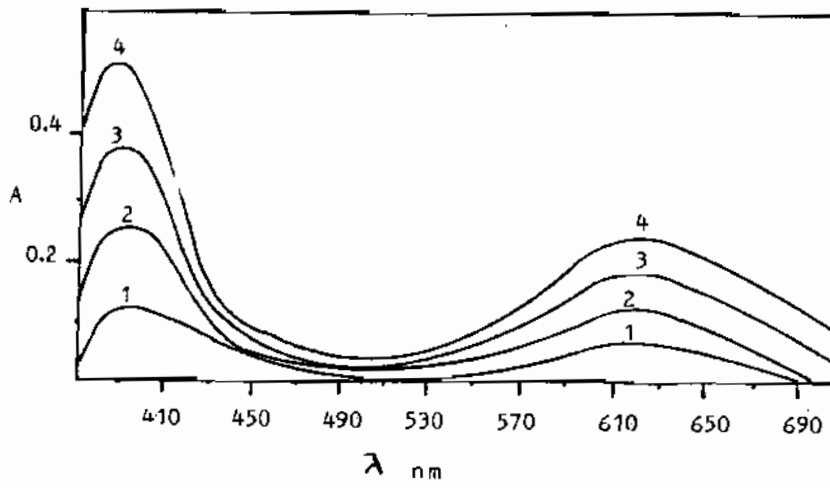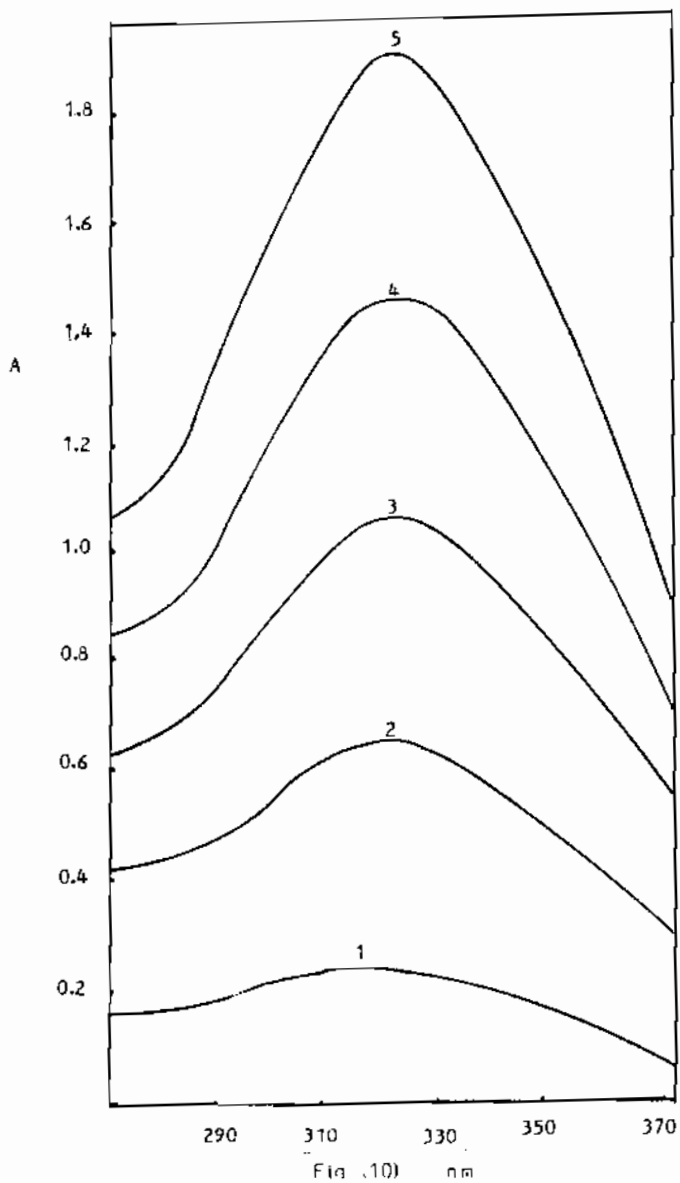

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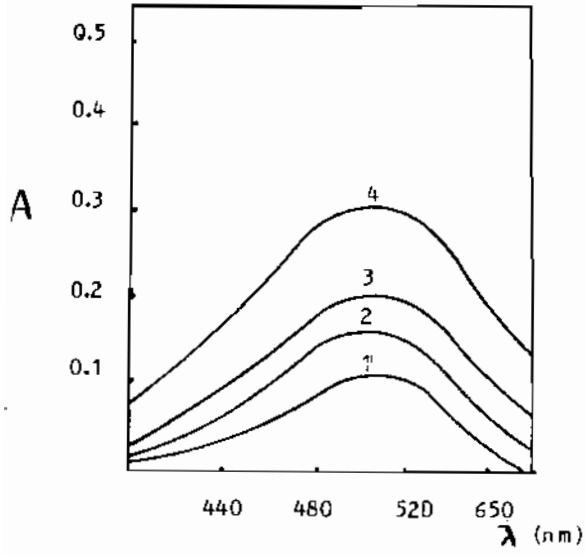
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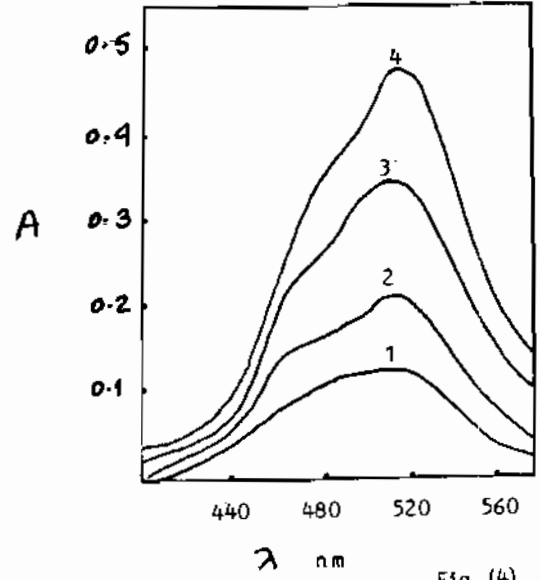
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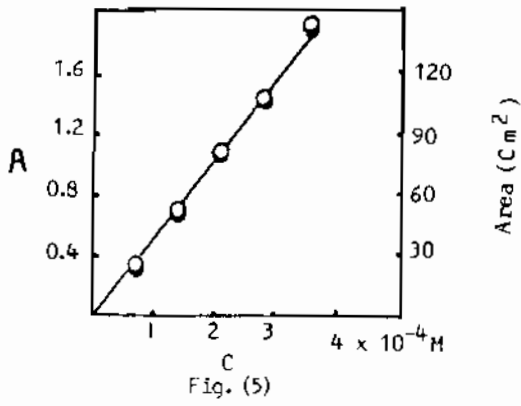
Fig. (5)

Fig. (6)

(Fig. (7)

Fig. (8)

Fig. (9)

Fig. (10)   nm