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

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طريقة تجريبية لتطوير تطبيق قانون ـ لامبرت التقدير الطيفي للمحاليل البسيطة

يتناول البحث طريقة تجريبية لاستخدام قانون بيرـ لامبرت ، ويتلخص في تعيين المساحة تحت المنحنى الناتج من أطياف محاليل قياسية عند تركيزات مختلفة بدلا من الامتصاصية ، وهذه الطريقة التجريبية أعطت علاقات خطية بين المساحات والتركيزات ، وتمت هذه الدراسة على بعض محاليل العناصر الانتقالية ومتراكباتها مع ١ ، ٢ ثنائي (بيتا أمينوايثوكسي) ايثان ن ، ن ، نَ ، نَ سلفونات الصوديوم ثلاثي حمض الخليك عند قيم أس هيدروجيني محددة .

وبمقارنة نتائج استخدام المساحات وكذلك الامتصاصية مع اختلاف التركيزات وبحساب الامتصاصية الجزيئية وجد أن الطريقة التجريبية المقترحة تعطى نتائج اكثر دقة وأوسع مجالا فى استخدام قانون بيرـ لامبرت وتعطى فرصة أكبر لتعيين التركيزات المتناهية فى الصغر .

ويخلص البحث الى اقتراح اضافة متكاملات الكترونية للأجيال المستقبلة من أجهزة قياس الطيف فى مجال الاشعة المرئية وفوق البنفسجية لتعيين المساحة تحت المنحنى لأقصى الامتصاصية الكترونيا للحصول على نتائج أفضل ، تمشيا مع نفس التطور الذى حدث لأجهزة الكروماتوجراف وأجهزة التحليل الاشعاعى المتعددة القنوات .

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 carried 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 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} 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 eonditions 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 $\bar{\epsilon}$ 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 $\frac{\sigma_n}{\bar{\epsilon}}$ % and $\frac{\sigma_{n-1}}{\bar{\epsilon}}$ % in case of taking area is generally less than those in case of taking absorbance. The table demonstrates, also, that the molar absorptivity $\bar{\epsilon}$, in case of taking area, is largly 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 wnere: (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^{--}

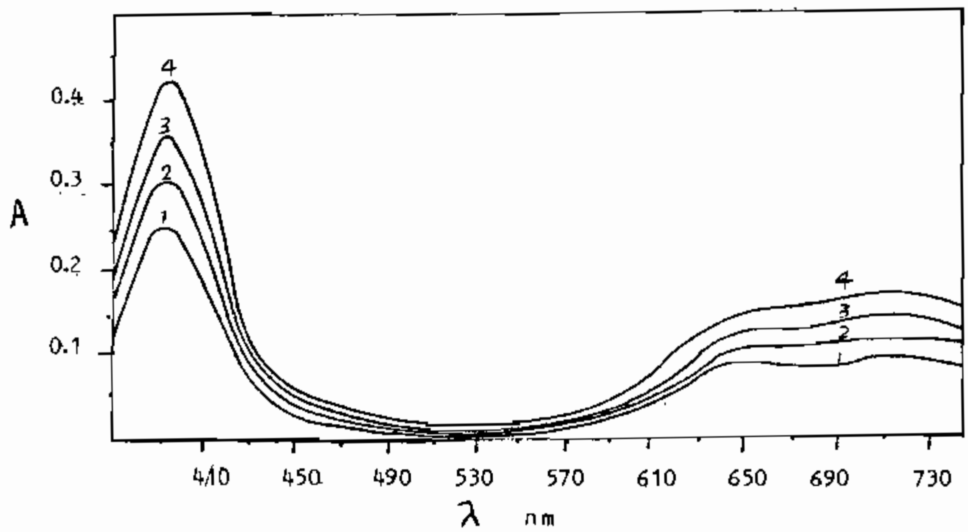
and Fig (10) for Ce $(SO_4)_2$

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

● The recommended theorem, viz: the relation betweeen 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}	$\frac{\sigma_n}{\epsilon}$%	$\frac{\sigma_{n-1}}{\epsilon}$%	$\bar{\epsilon}$	$\bar{\sigma}_n$	$\bar{\sigma}_{n-1}$	$\frac{\bar{\sigma}_n}{\bar{\epsilon}}$	$\frac{\bar{\sigma}_{n-1}}{\bar{\epsilon}}$%
$NiCl_2$	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



A
0.4
0.3
0.2
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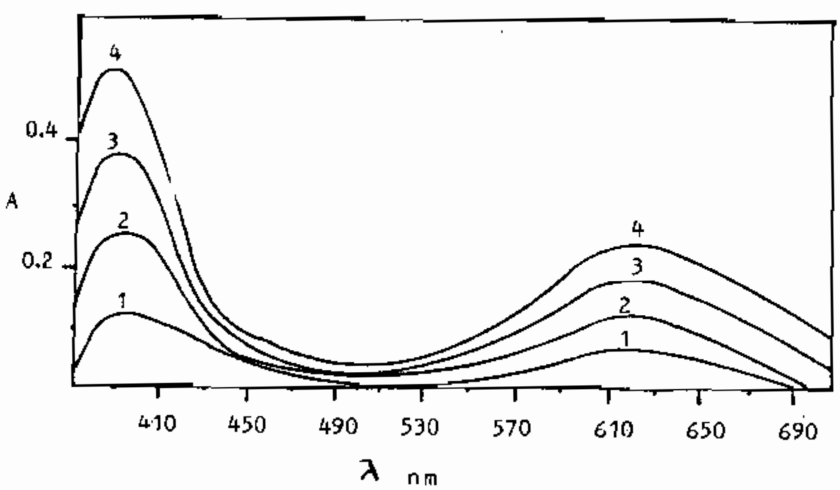
410
450
490
530
570
610
650
690
730
λ nm
1
2
3
4

Fig. (1)



A
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0.2
410
450
490
530
570
610
650
690
λ nm
1
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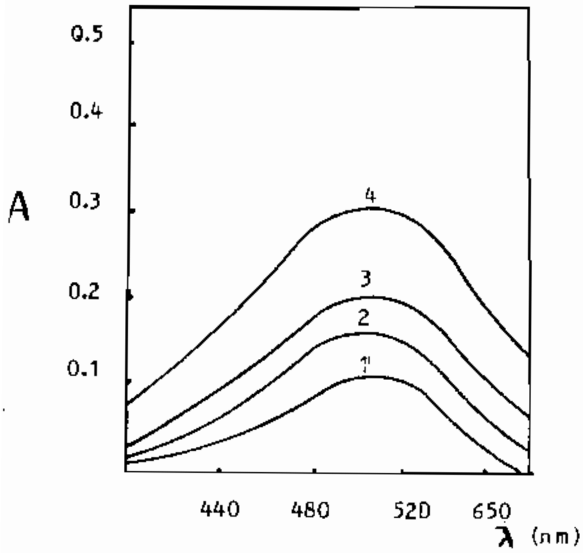
4

Fig. (2)



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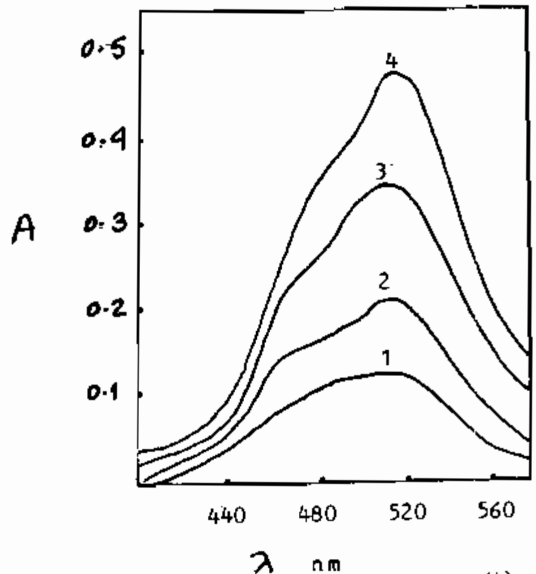

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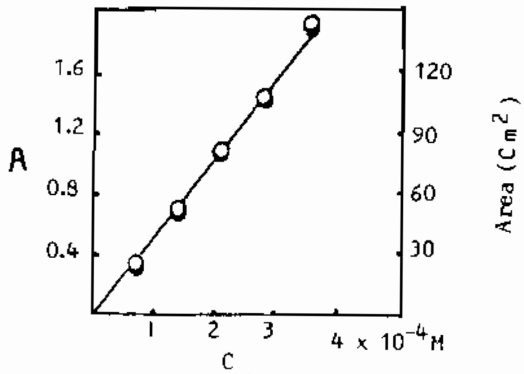


Fig. (5)

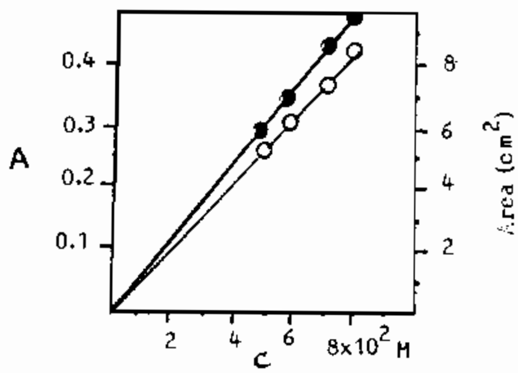
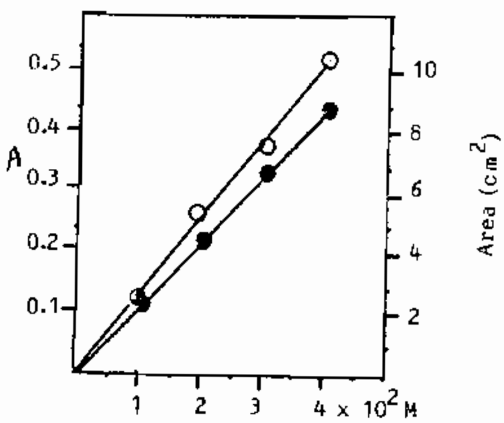
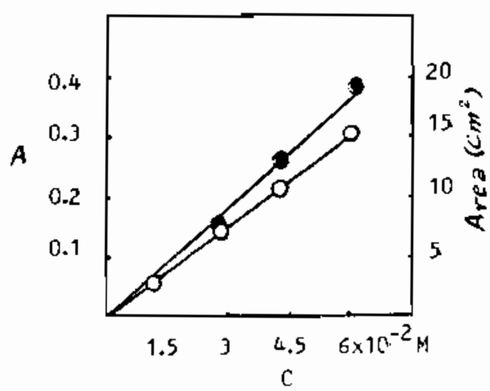


Fig. (6)



(Fig. (7)



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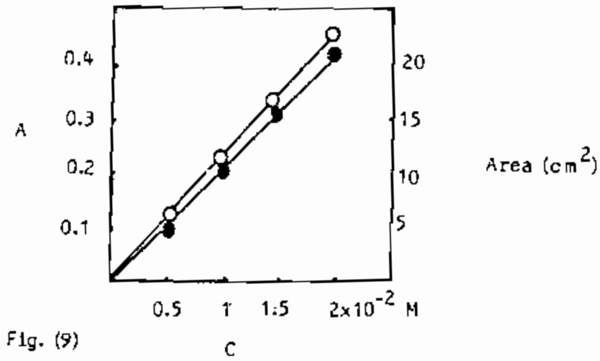
A
0.4
0.3
0.2
0.1
20
15
10
5
Area (cm^2)
0.5
1
1.5
2x10^{-2} M
C

Fig. (9)

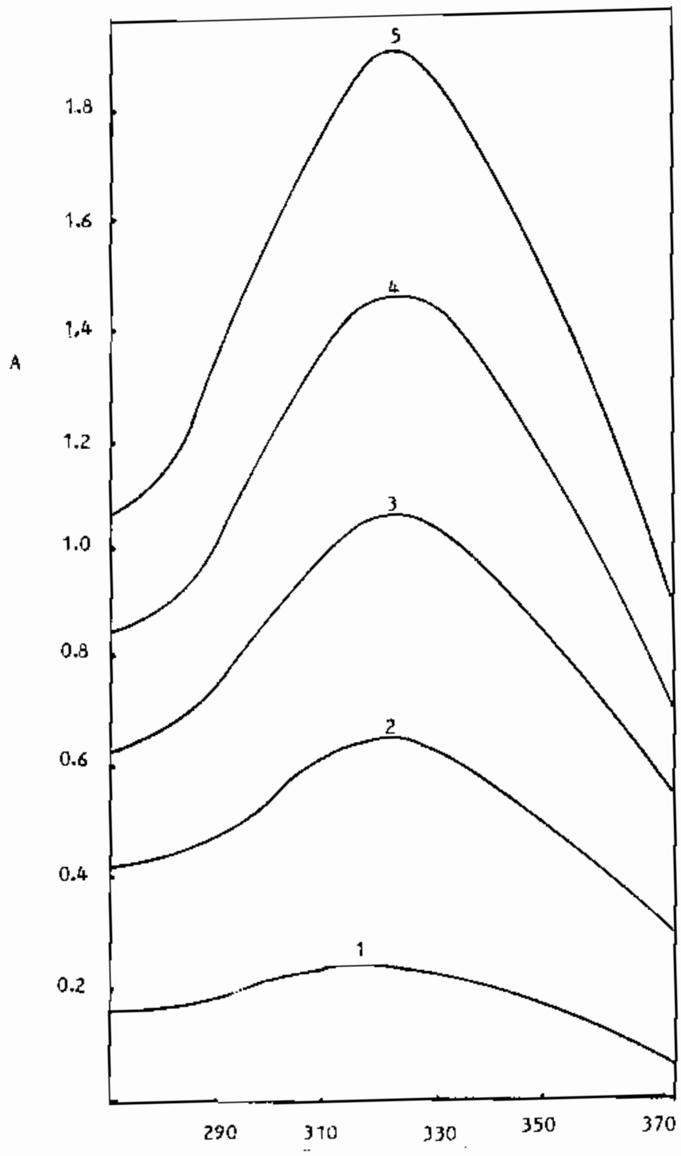
A
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
5
4
3
2
1
290
310
330
350
370
nm

Fig. (10)