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دراسة مشتقة طيف الاشعة فوق البنفسجية لعدد من قواعد شيف في الايثانول المطلق

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المخلص

نظراً للأهمية البايولوجية والصناعية لمركبات قواعد شيف فقد تم تطبيق طريقة طيفية جديدة لدراسة وتقدير مركبات من قواعد شيف متكونة من التفاعل بين مركبات الالديهايد والباراتولوين سلفوناميد بالاعتماد على اطياف هذه المركبات عند المرتبة صفر والمشتقة الرابعة حيث سجلت اطياف قواعد شيف التالية : [(بنزايليدين للمركب I) و(3, 4 – ثنائي ميثوكسي بيزايلدين للمركب II) و(2, 6 – ثنائي كلورو بنزايلدين)] مع الباراتولوين سلفوناميد في الايثانول المطلق وكذلك التقدير الكمي لهذا القواعد من خلال رسم المنحنيات القياسية لكل منها وايجاد حدود التقدير العليا والدنيا والتي تتبع قانون بير – لامبرت وايضاً اختبار مدى تطبيقية الطريقة للتقدير الكمي لهذه المركبات وحساب قيم معامل الارتباط R^2 والنسبة المئوية للأنحراف القياسي R.S.D والتي اظهرت ان هذه الطرائق ذات حساسية ودقة عاليين.

الكلمات المفتاحية: fourth order , Schiff base , p-toluenesulphonamid

Derivative UV-Spectroscopic Studies of some Schiff Bases in Absolute Ethanol

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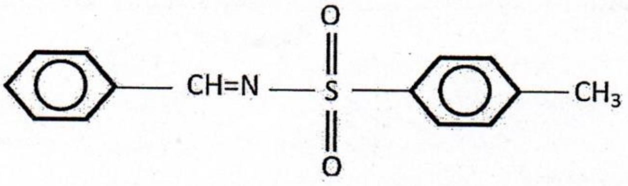
ABSTRACT

According to the biological and industrail importance of Schiff bases compounds , a new simple and accurate UV spectrophotometric method was established for the studied and determination of the Schiff bases compounds formed from the reaction between aromatic aldehydes compounds and P-toluenesulphonamide , depending on the zero and fourth derivative mode techniques . The zeroth and fourth order derivative spectra of the Schiff bases : [benzylidine (compound I) , 3, 4 – dimethoxybenzylidine (compound II) and 2 ,6 – dichorobenzylidine (compound III)] p-toluenesulphonamid , were recorded in absolute ethanol for series of different concentration solutions . The calibration curves were ploted which result in astraight lines obeying Beers – Lambert law with R^2 values and R.S.D for compound I . II and III . These values indicate that these techniques having good sensitivity and precision for the quantification of these Schiff bases .

Keywords: fourth order , Schiff base , p-toluenesulphonamid

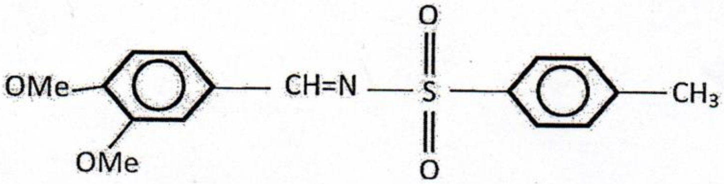
INTRODUCTION

The Schiff bases are very important organic compound , they have different biological activities [1] also they are known to exhibit awide variety of pharmacological properties , antibacterial, antifungal and anticancer [2] and they are widely used for industrial purposes beside the biological activities [3] . Alarg number of research works have been reported about study of Schiff bases compounds like : synthesis , spectroscopic studies depending on IR , UV –Visible spectroscopy , H ^{1}N M R , C^{13} NMR and mass spectra of new azo ligands Schiff base and amines derived of 5-phenylazo -2- hyaroxy bezaldehyde [4]. And about spectrophotomertric determination of these compound such as spectrophotomertric determination and spectroscopic studies on Schiff base[5] . Dervivative UV- spectroscopy has been widely used as a tool for quantitative analysis , characterization and quality control in the agricultural , Pharmaceutical and biomedical fields [6]. So that many researches have been carried out in the field of UV-derivative. For example : second, third and fourth order derivative UV- spectrophotomertric methods have been developed and validated for the estimation of abacavir sulphate in bulk and it's tablet formulations, the bulk drug and Pharmaceutical formulations of abacavir sulphate is easily accessed by this method [7]. Sensitive spectrophotomertric method has been developed for the quantitative estimation of famotidine (FAM) and ibuprofen (IBU) individually as well as combined dosage form . First order derivative spectrophotomertric method involves the measurement of absorbance of one drug at zero crossing point of other drug , 249nm and 263.6 nm was selected for the estimation of IBU and FAM respectively , linear ranger was found 4-20μg/ml and 20-60μg/ml with (R^2 = 0.9987,% cv=0.32 to 1.49 and R^2 = 0.9930,% cv = 0.71 to 1.50) for FAM and IBU respectively . LOD for FAM and IBU were found to be 0.252 μg/ml and 10μg/ml respectively . The proposed walidated method was successfully used for the quantitative analysis of synthetic mixture [8]. Also derivative spectrophotomertriy technique become very useful in the field of kinetic studies[9]. U.V. Derivative spectra studies of some schiff's bases of amino acids complexes were recorded by first and second order derivative for the complexes of Schiff bases derived from leucine amino acid with sodium -3- acetylpyridine (Nal1) and sodium acetoacetanilide ($NaHl_2$) with Co and Ni and their direct determination [10]. In this work and for the first time the fourth order derivative were studies for the compound of Schiff bases , benzyylidine p-toluenesulphonamid (I) , 3,4 – dimethoxybenzylidine p-toluenesulphonamid (II) and 2,6 –dichlorobenzylidine p- toluenesulphonamid (III) and their direct quantification by UV derivative spectroscopic technique.



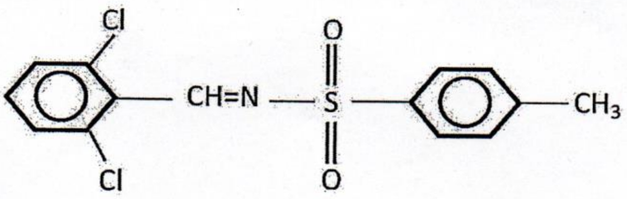
(I)

benzylidine p-toluenesulphonamide



(II)

3,4-dimethoxybenzylidine p-toluenesulphonamide



(III)

2,6 dichlorobenzylidine p-toluenesulphonamide

EXPERIMENTAL

Synthesis of compound (I-III): [11]

Materials :

All aldehydes [benzaldehyde,2, 6 dichlorobenzaldehyde and 3,4 dimethoxybenzaldehyde] are of pure type and were used as freshly distilled for liquid phase, p-toluenesulphonamide obtained from fluka absolute methanol obtained from hopkin and williams .

Proparation of the Schiff base compound (I-III)

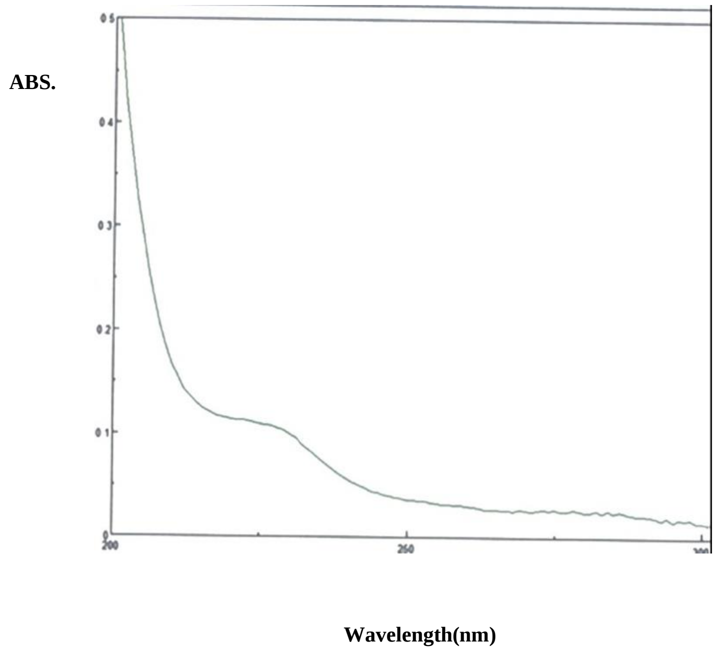
To a solution of aromatic aldehyde (0.02 mole) in (30 ml)of methanol (99.5 %) . p-toluensulphonamide (0.02 mole) was added, the reaction mixture was refluxed for, 24 hours, the solvent was then evaporate under vacuum and the solids was collected and recrystallized from xylend.

Intrumentation

All the U.V.spectra were recorded using UV- visible spectrophotometer shimadzu UV-1650 PC using 1×1×3 Cm matched quartz cells, for UV-spectra measurement (25) ml (10^{-2} M) solution in ethanol were prepared by dissolving (0.0647gm), (0.0797gm) and (0.0820gm) from compound I , II and III respectively and by appropriate dilution the solutions 10^{-3} M, 10^{-4} M and 10^{-5} M in ethanol were prepared .

RESULTS AND DISCUSSION

The zero order UV.spectra of the Schiff bases (I,II and III) were recorded in absolute ethanol solvent shows an absorption maxima and their molar extention coefficient calculated as shown in Fig (1) , Table (1). And the UV absorption spectrum of the (blank) absolute ethanol show as :



From the above spectrum it is clear that there is no effect of the UV.spectra of the blank for the compounds under study .

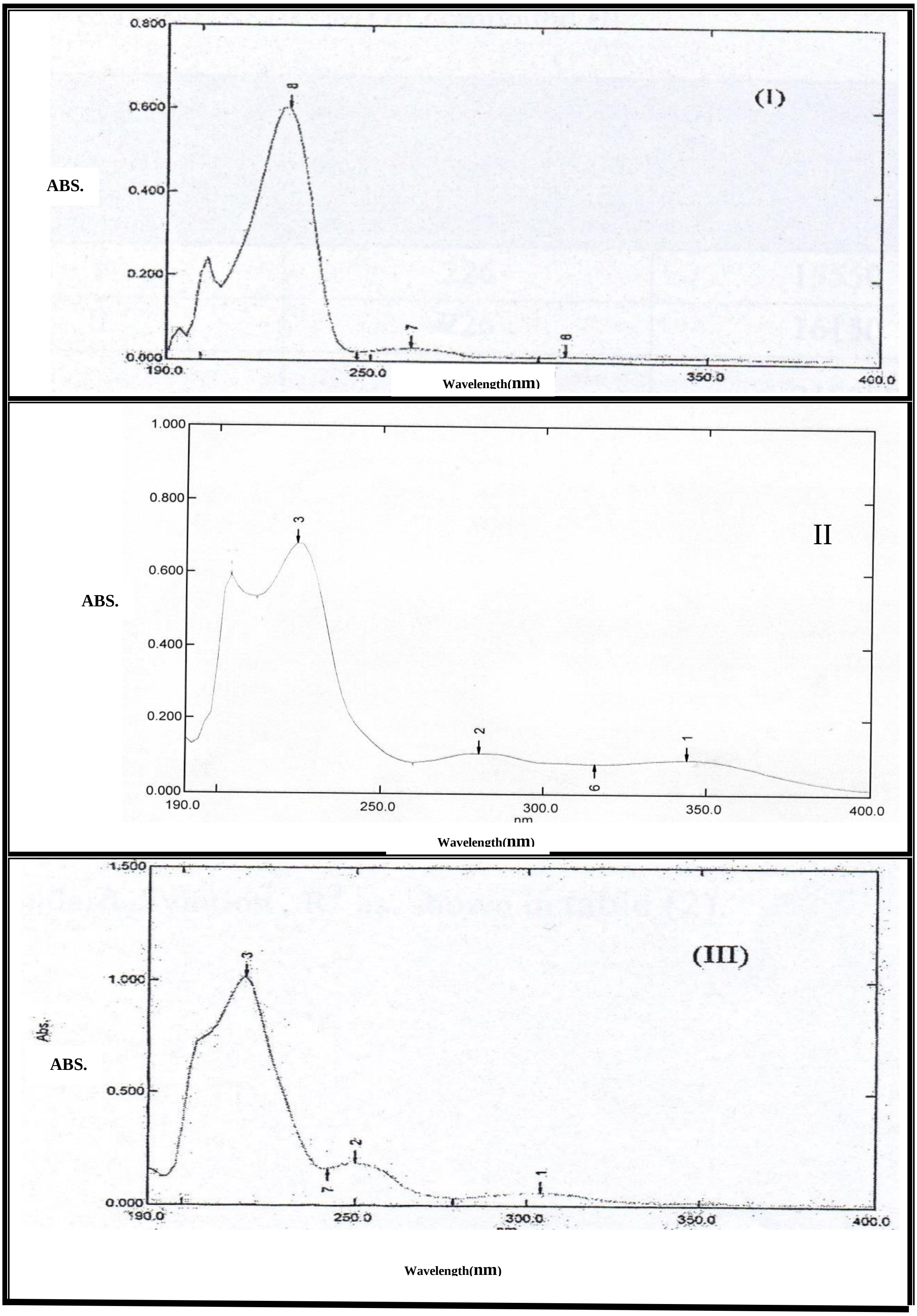
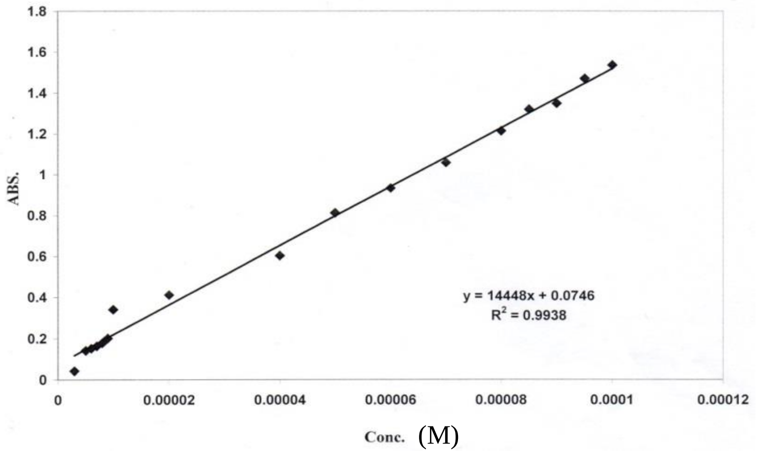


Fig (1) : The UV absorption apectrum of (4×10^{-5} M) of compound (I,II and III) In absolute ethanol (zero - order) .

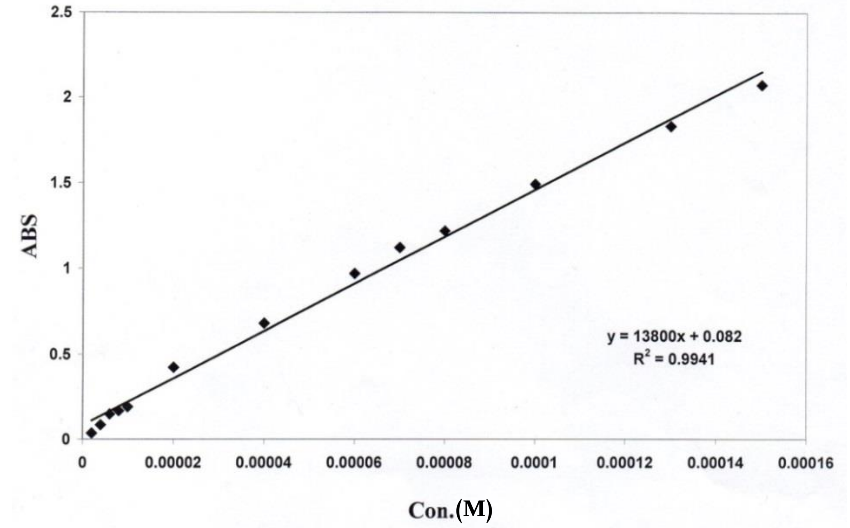
Table(1): The UV absorption for solution (6×10^{-5} M) fo the compound I & II and (8×10^{-5} M) fo compound III .

compound	**Wavelength of absorption (nm)**	**εmax Lit.mole^{-1}.cm^{-1}**
I	226	15550
II	226	16150
III	220	21800

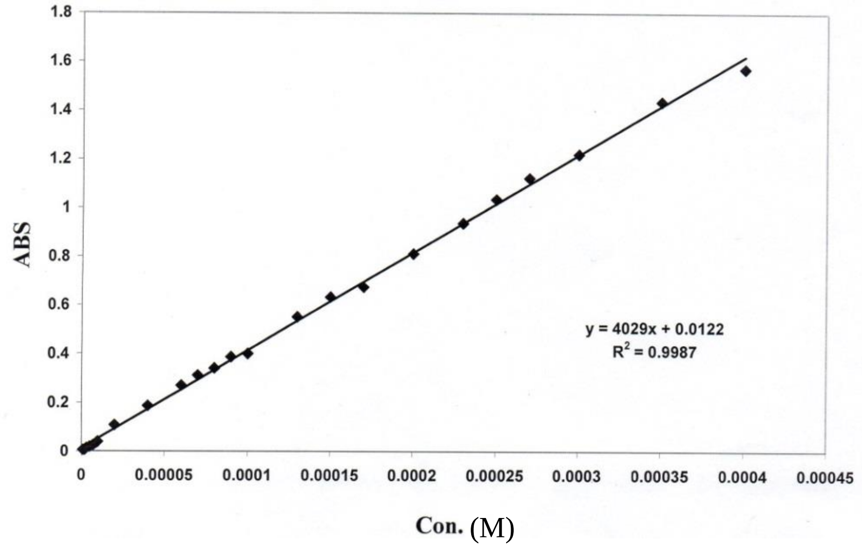
For the quatification of these Schiff based according to the zero- order obsorption spectra were accomplished bases on the measured absorbances at (226nm) for compound I & II and at (220nm) for compound III , the measured absorbances were ploted versus the molar concentration and the result shows a straight line obeying Beers-Lambert law as shown in Fig(2)within a concentrationranges and relative stander deviation , R^2 as shown in Table(2).



Compound (I)



Compound (II)



Compound (III)

Fig(2): The relationship between the values of absorbance and molar concentration in absolute ethanol of compound I,II and III.

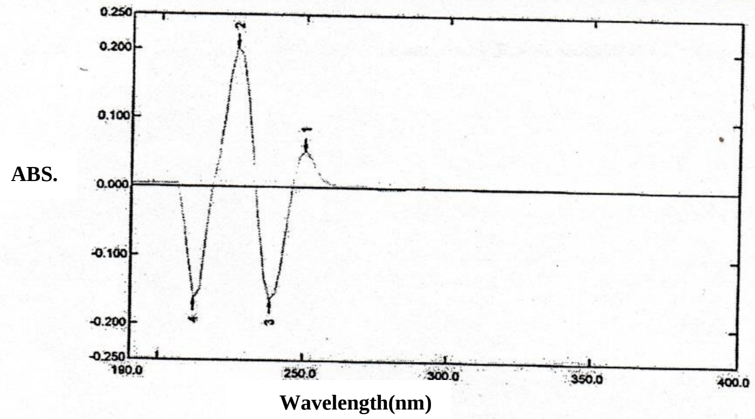
From these relationship , its clear that the straight line abeying Beer's Lambert law within the range of (3×10^{-6} – 1×10^{-4} M) for compound I, (2×10^{-6} – 1.5×10^{-4}) for compound II and (1×10^{-6} – 4×10^{-4} M) for compound III .

Table(2): The values of lower and upper determination limits , R^2 and R.S.D for the compounds of Schiff bases I,II and III .

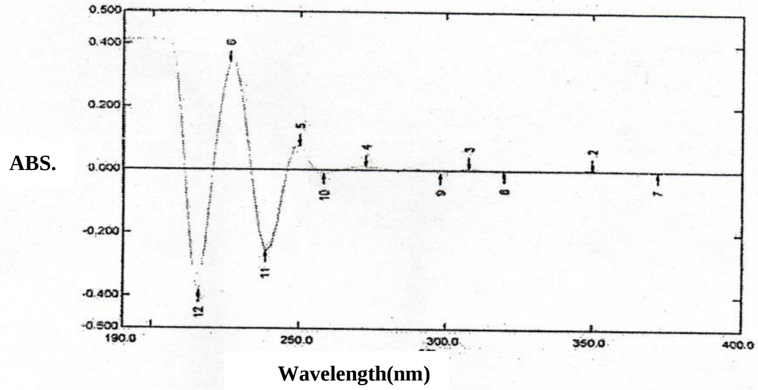
compound	**Lower determination limit µg / ml**	**Upper determination limit µg / ml**	**R^2**	**R.S.D %**
I	0.77	25.9	0.9938	1.8
II	0.63	47.8	0.9941	3.8
III	0.32	131.2	0.9987	0.6

The fourth order derivatives spectra of compounds I,II and III were recorder and show absorption maxima at (226nm) for compounds I & II and (220nm) for compound III . Compounds I & II show main positive peak at (226nm)and two satalits at each side for these peaks , for compound III the main positive peak is at (220nm) and two satalites at each side of these peak fig(3).

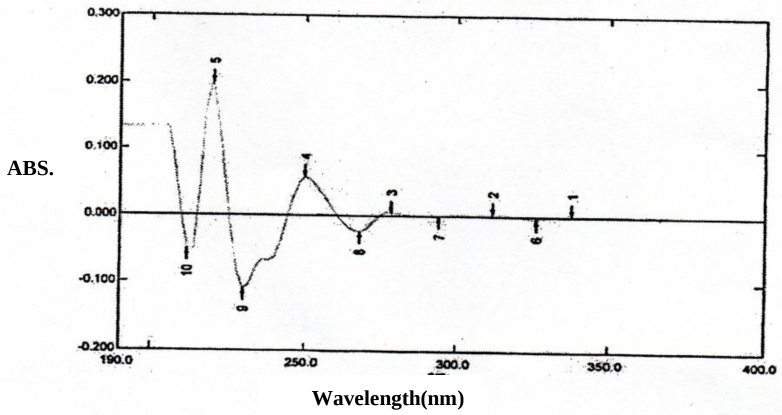
The presence of substituent in compound II and III effect the values of the determination limits due to their behavior electronically as shown in table(2).



compound (I)



compound (II)



compound (III)

Fig (3) : UV : absorption spectra of fourth order derivatives for compounds I,II and III in absolute ethanol

The quantification of these compounds according to the measured absorbance at these maxima was done and the result in straight line relation within a concentration range , R^2 and R.S.D as shown in Fig (4) , Table (3)

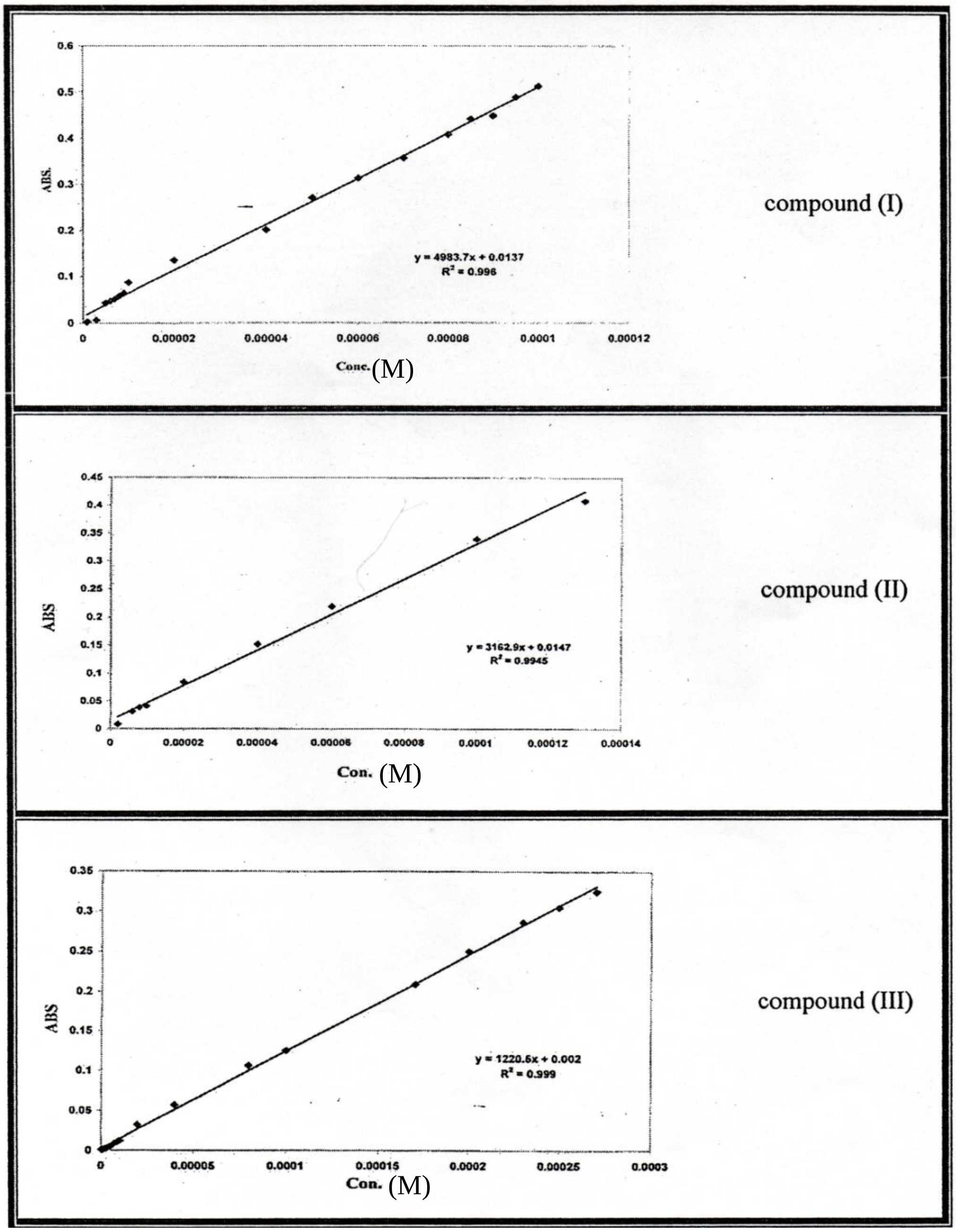


Fig (4) : the fourth order derivatives calibration curve of the compounds of Schiff bases I,II and III at different concentration .

From the calibration curves for the compounds in Fig (4) , we can conclude thatthe straight light obeying Beer's lambert within the range of (9×10^{-7} -1×10^{-1} M) for compound (I) , ($2 \times 10^{-6} – 1.3 \times 10^{-4}$ M) for compound (II) and ($7 \times 10^{-7} – 2.7 \times 10^{-4}$ M) for compound (III).

Table (3) : the value of lower and upper determination limits , R^2 and R.S.D for the fourth order derivative spectra for compound I,II and III in absolute ethanol .

Compound	**Lower determination limit μg / ml**	**Upper determination limit μg / ml**	**R^2**	**R.S.D%**
I	0.23	25.9	0.9960	0.9
II	0.63	41.47	0.9945	0.1
III	0.22	88.56	0.9990	0.2

From Table (2) and (3) it's clear that the fourth order derivative technique is more relable for the quantification of compound I and III specially the lower determination limit , while the zero order derivative technique is preferable for compound II due to the wider range of determination .

The accuracy and precision of the method were detected through the preparation of three different concentration solutions (each five times) and the measurement of their absorbance's by the zero and fourth order derivative for the three compounds the results are shown in Table [4,5,6].

Table (4) : Accuracy and precision of the study the compound (I) in absolute ethanol (zero and fourth order).

Zero-order			
Taken μg /ml	**Found μg /ml**	**Recovery %**	**Error**
3.36	3.62	107.9	7.9
10.61	11.13	104.9	4.9
24.08	23.54	97.7	-2.3
Fourth-order			
Taken μg /ml	**Found μg /ml**	**Recovery %**	**Error**
3.10	3.36	108.3	8.3
10.36	10.61	102.4	2.4
23.31	23.56	101.0	1.0

Table (5) : Accuracy and precision of the study the compound (II) in absolute ethanol (zero and fourth order).

Zero-order			
Taken µg /ml	**Found µg /ml**	**Recovery %**	**Error**
3.19	2.87	89.8	-10.2
15.63	13.71	87.8	-12.2
41.47	41.47	100	0
Fourth-order			
Taken µg /ml	**Found µg /ml**	**Recovery %**	**Error**
3.12	3.12	100	0
15.31	14.99	97.9	-2.1
41.15	39.55	96.1	-3.9

Table (6) : Accuracy and precision of the study the compound (III) in absolute ethanol (zero and fourth order).

Zero-order			
Taken µg /ml	**Found µg /ml**	**Recovery %**	**Error**
2.03	2.03	100	0
15.08	14.76	97.8	-2.2
54.77	49.2	89.2	-10.8
Fourth-order			
Taken µg /ml	**Found µg /ml**	**Recovery %**	**Error**
2.14	2.14	100	0
15.08	16.07	106.5	6.5
56.08	56.41	100.5	0.5

The result indicate that both methods (zero and fourth order) could be applicable for the quantification of these compound with a good recovery and precision .

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