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PreparationandSeparation of some P-cresol derivatives by Gas–liquid chromatography

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Abstract

The first part of this study involve preparationand identification of somep- cresol derivatives $C_{14}H_{14}N_2O$ (4-MePAMeP), $C_{13}H_{11}ClN_2O$ (4-CPAMeP),$C_{14}H_{14}N2O_2$(4-OMePAMeP).In the second part including the study of gas chromatographic behavior of theprepared compounds on liquid- stationary phases fused silica (BP10),Zebron (FFAT),Polysiloxane (OV-5) capillary column by using Gas Chromatography apparatus with Flame Ionization Detector FID,N_2- as carrier gas with optimal flow rate30 cm^3/min ; with $(10)^0$Cincrement depend on maximum temperature operation on column and the temperature of the column inlet and detector were higher than the separation column by $(25,50)^0$C respectively .The results indicate that the chromatographic behavior was normal ,showing decrease of specific retention volume with increase of column temperature ,and a linear relation between logarithm of specific retention volume and the reciprocal of absolute temperature appears depending onClausius –Clapeyron equation , the ΔS^0 , ΔH^0 , ΔG, were calculated after that the resolution (R_S) ,number of theoretical plates(N) andheight equivalent to theoretical plate(HETP) were also calculated.

Keyword: P-cresol derivative, Gas Chromatography, Liquid stationary phase.

الخلاصة

تضمن الجزء الأول من البحث تحضير وتشخيص بعض مشتقات الآزو للباراكريزول (4−MePAMeP)$C_{14}H_{14}N_2O$, (4−CPAMeP)$C_{13}H_{11}ClN_2O$, (4−OMePAMeP)$C_{14}H_{14}N_2O_2$. إماالجزء الثاني شمل دراسة التصرف الكروماتوغرافي الغازي للمركبات المحضرة على الاطوارالسائلة الثابتة منصهر السليكا (BP10),زيبرون (FFAT), فنيل متعدد السيلوكسين (OV−5) ,وباستخدام كاشف التأين اللهبي المثبت في جهاز كروماتوغرافياالغاز والنيتروجين كغاز ناقل وكانت سرعة الجريان المثلى له (30) سم^3 / دقيقة. واستخدم لدراسة المركبات المحضرة مدى من درجات الحرارة بزيادة تدريجية (10) م^o وحسب درجة الحرارة القصوى للعمود, اما مدخل العمود ودرجة حرارة المجس كانت أعلى من حرارة عمود الفصل (25, 50) م^{o}على التوالي .

بينت النتائج ان السلوك الكروماتوغرافي كان اعتياديا اذ يعني ذلك النقصان في حجم الاحتجاز النوعية مع زيادة درجة حرارة العمود كما تم الحصول على العلاقة الخطية بين لوغاريتم حجم الاحتجاز النوعي ومقلوب درجة الحرارة المطلقة اعتمادا على معادلة كلاسيوس–كلابيرون,ومن هذه العلاقة تم حساب المعطيات الثرموديناميكية ΔG, ΔH^0, ΔS^0كما تم حساب عامل الفصل(R_S),عدد الصفائح النظرية(N), الارتفاع المكافئ لصفيحة نظرية واحدة(HETP).

Introduction

The popularity of gas chromatographic method is due to the ability to separate and quantitatively determine mixture of organic substances and the separation mechanism depend on the selective phase, rate of carrier gas, temperature, column loading(1,2). Gas chromatography–mass spectrometry was used for the determination of 16 priority polycyclic aromatichydrocarbons (PAHs)(3). Also, they have been usedazo compounds free radical cross-linking and the effects that these free radical generators have on commercially available stationary phases are described. Characteristics of the stationary phases such as chain length and functional groups and their roles in the cross(4-6) .A new micro extraction technique with gas chromatography–mass spectrometry was developedfor determination of trace chlorophenols (CPs) in landfill (7).Many methods have been developed todetermine organic compounds including gas chromatography (8, 9).The analysis of 3-alkyl-2-methoxypyrazines in Vitisvinifera grape must or wine at level failed in several situations when applying a one-dimensional gas chromatography(10). A method has been developed to measure levels of 3-amino-1-methyl-6-phenyl-imidazo [4, 5-b] pyridine in urine and feces(11). Gas chromatography is an important method of analysis for complex mixtures of volatile and semi-volatile organic compounds for several decades (12). Several published chromatograms two peaks for azo-dyes,there areobserved (13, 14). The origin of the “fast peak” is described as a “minor isomer ofazo -dyes” in only one publication(14).

Experimental

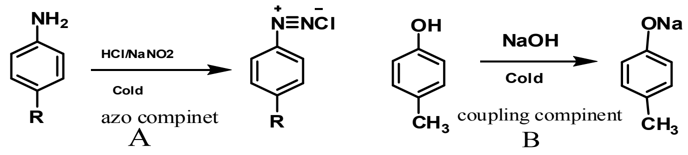
Chemicals andInstruments

All chemicals used were supplied by Merck, Fluka AG and BDH chemicals with high degree of purity. Double beam UV-Vis Spectrophotometer, Shimadzu 700 (Japan),FTIR spectra were recorded on Shimadzu– FTIR 8400using KBr discs, Melting point were determined in open capillaries on Thomas Hoover apparatus9300 -U. K. and Shimadzu GC-2014 (Japan)Gas chromatography equipped withFlame Ionization Detector (F.I.D) is used.

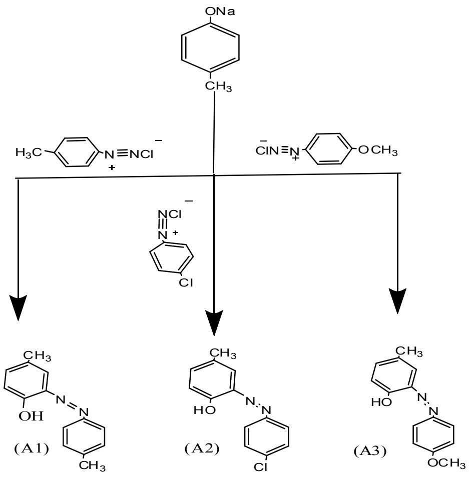
Experimental Procedure

Preparation of 2-[(4-Substitutid Phenyl) azo] 4-Methyl Phenol

The titled azo derivatives from p-cresolwere prepared according to literatures (15).To solution of (2.1 g) of [p-Toluidine, P-Chloroaniline, P-Anisidine] in (5 ml) of HCl conc. was added a solution of (1.4 g) of $NaNO_2$ dissolved in (25ml) of Water with stirring and cooling. The product is calledDizonium salt (A) to which a solution of (4.18 ml) of p-Cresol with (3 g) of NaOH is added with cooling this mixture is called coupling component (B) ,on mixing (A) and (B) . a resultant dyes was formed, washed with water and dried then was purified by recrystallizationwith ethanol. FTIR Spectra data of compounds are listed in table no (2).



$R=CH_3, OCH_3, Cl$

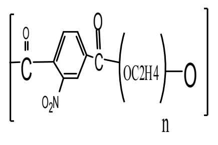
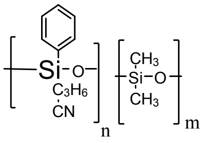
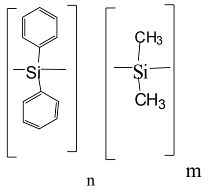


Capillary columns

The first column was a 30m×0.25 mm I.D.×0.25 µm film thicknessZebron (FFAT), the second column was a 30m×0.25mm I.D.×0.25µm film thicknessFused silica (BP10),and the third column was a 60m×o.32mm I.D×0.25µm film thicknessPolysiloxane (OV-5).

The detail characteristics of liquid phases are listed in table (1).

Table 1: Characteristics of the used Liquid Stationary Phases.

Liquid phase	Composition	Formula	Column dimension	Temperature Range(M.O.T)	Polarity
ZB-FFAP	Nitroterephthalic Acid Modified Polyethylene Glycol		0.25mmI.D 0.25-md.f	40 to250/260 C°	High Polar
F.S BP10	14%Cyanopropyl phenyl poly siloxane		0.25mmI.D 0.25-md.f	-20 to280/300 C°	Moderate Polar
OV-5	5%Diphenyl 95%Dimethyl polysiloxane		0.53mmI.D 1.5-md.f	-60 to310/330 C°	Non-polar

Studying the effect of temperature on the chromatographic behavior

Mixtures were prepared by weighing(0.3gm) of each compound and were blended in the volumetric flaskindividually. From mixture (0.1-0.6) µL were injected by Hamilton Syringe .The components of each mixture were run individually to determine the order of elution of these components .The analysis of each mixture were repeated twice and the reproducibility was with ± 1 per cent. All the optimum conditions were kept throughout isothermal column temperatures ranged from(200-240)^{0}C for F.S (BP10), temperatures ranged from (230-240)^{0}C for Z-B (FFAT) and temperatures range from (190-230)^{0}C for OV-5.

Results and Discussion

Spectrophotometric studies:

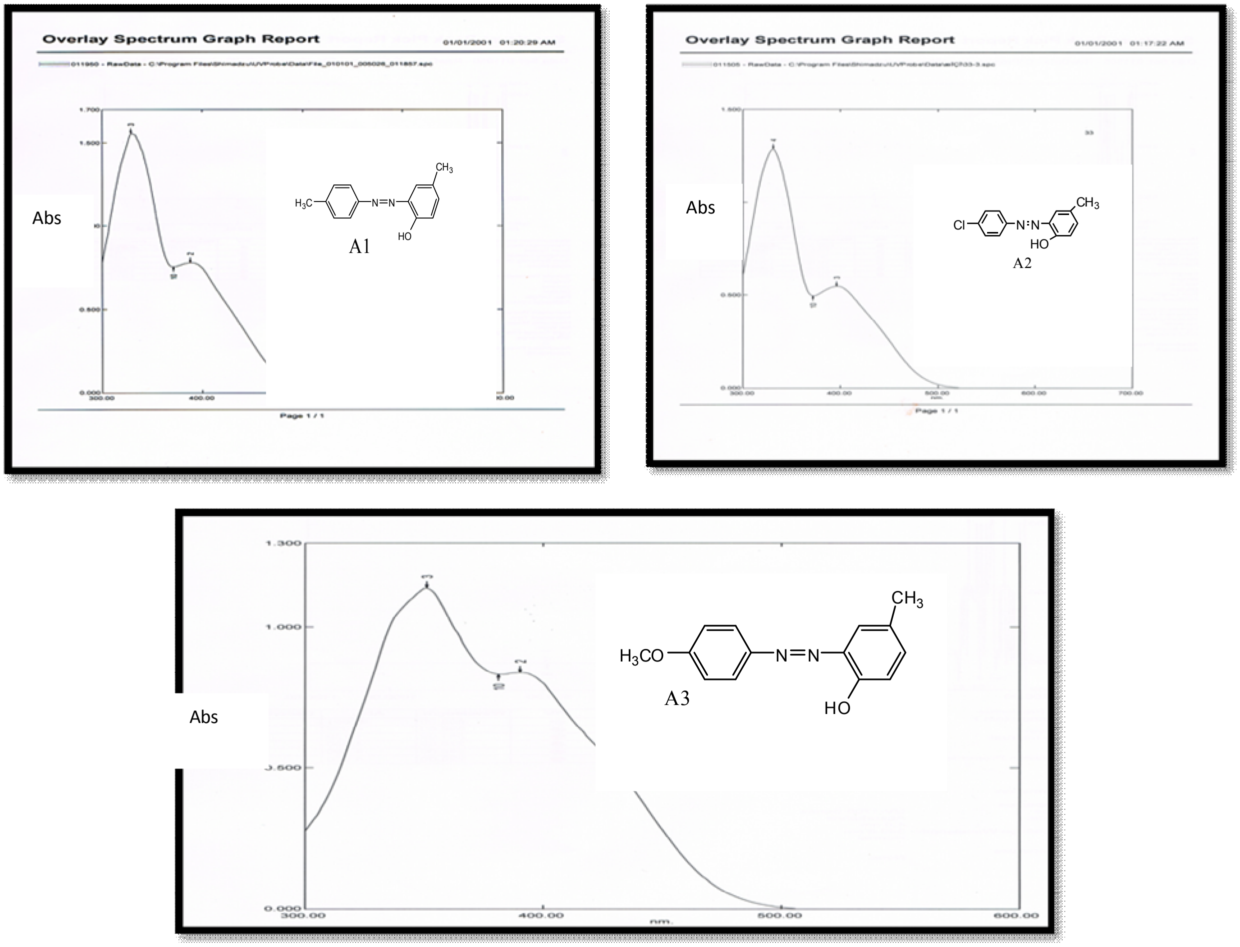


Fig (1): UV -Vis Spectrumfor organic reagent (A1, A2, A3) in ethanol solvent.

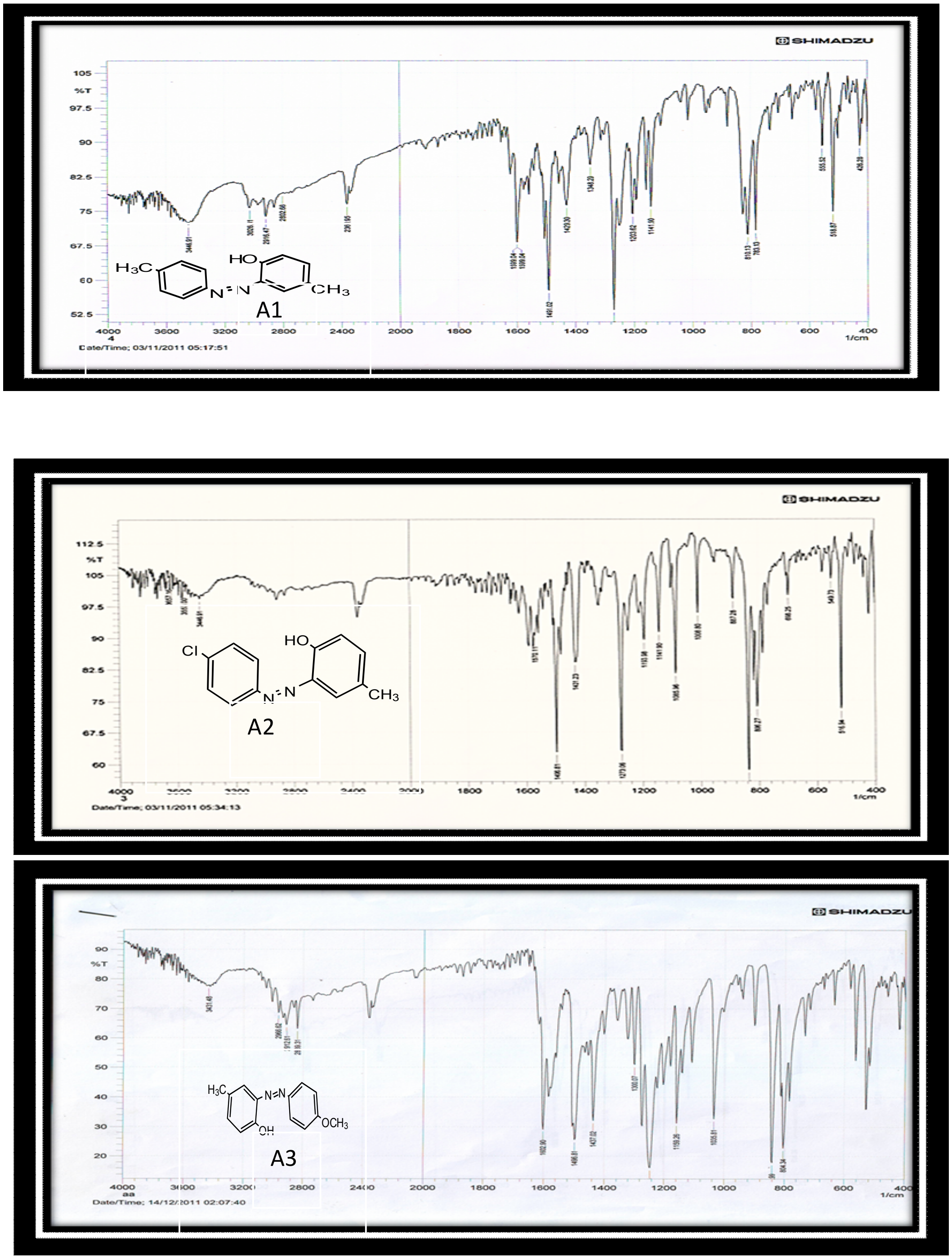


Fig (2): FTIR spectra for organic reagent (A1, A2, A3).

Table 2: FTIR spectra of the prepared compounds in this work (part 1)

Comp No.	ν(OH)	ν(N=N)	ν(C=C) Aromatic	ν(C-H) Aromatic	ν(C-H) Aliphatic	Other
A1	3446	1491	1599	3025	2916	-
A2	3421	1496	1575	3030	2914	Cl(1084)
A3	3431	1496	1602	3060	2996	νc-o-c (1159)

Qualitative study:

The retention volume is an important characterization property in chromatography. It is often used for identification and it is normally determined from chromatogram by using the following equation:

$V_R = t_R.F_C$………..(1)

Where (t_R) is the retention time; and (F_C) is the volume flow rate of the carrier gas at the temperature of the column and its outlet pressure.When use a compressibility correction factor (j) this correct retention volumes is defined as net retention volume.

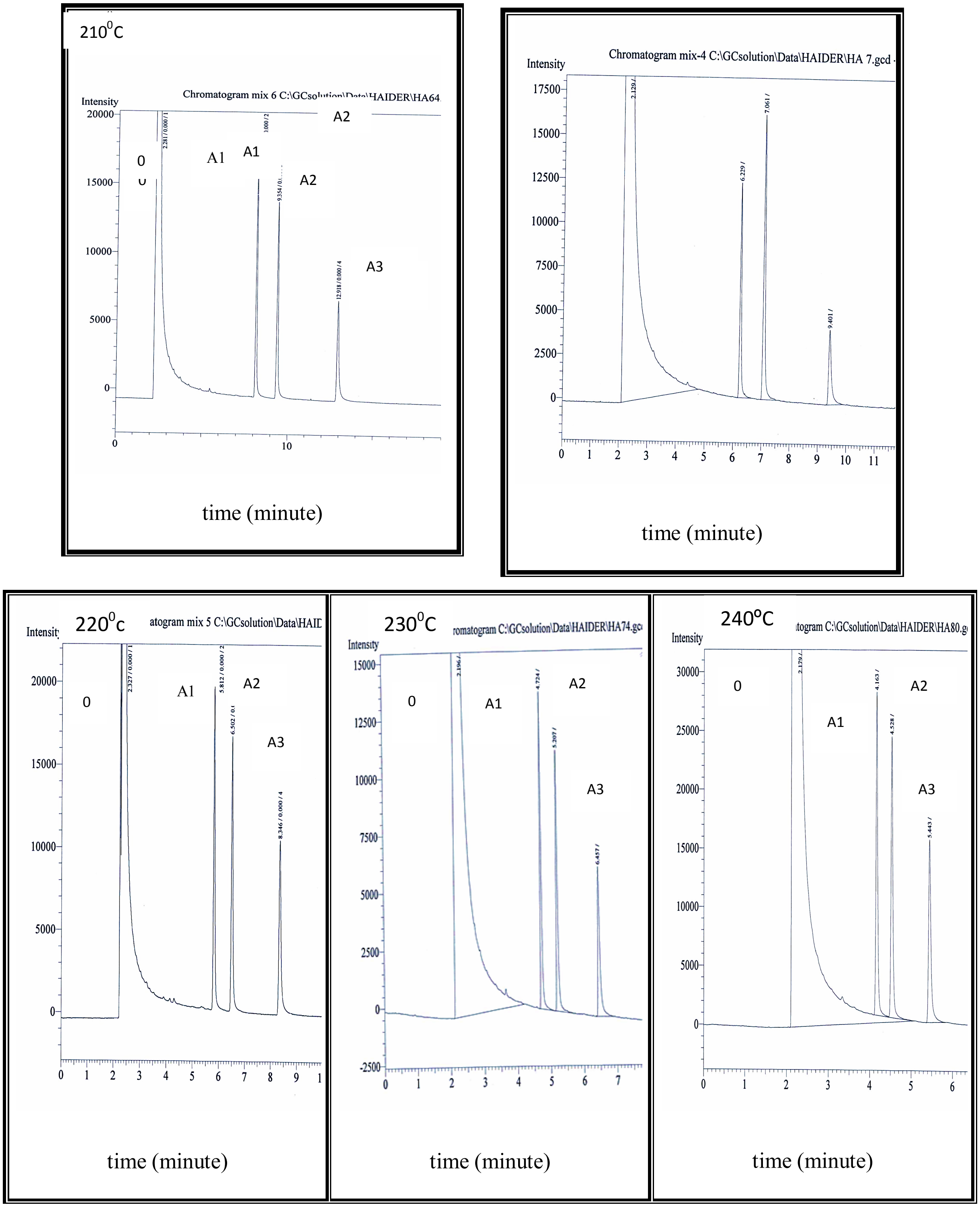
$V_N = V_R.J$ ……….(2)

Where $J=3/2[\{(Pi/Po)^2 -1\}$

$/ \{(Pi/Po)^3-1\}]$ …………...(3)

Where (Pi) and (Po) is the pressure at inlet and of the outlet of the column,

In order to take into account the weight of liquid phase in column,the specific retention volume is defined.$V_g=V_{N/}/W_{L.}\ 273/T$



Fig(3): Separation of azo derivatives (A1,A2,A3) where solvent: ethanol (0) .Stationary phase: fused-silica BP10 capillary column (30m ,0.25 mm. I. D, 0.25µm film thickness); injector temp.: 270C; total flow rate: 30 ml min -1, split ratio:1:50

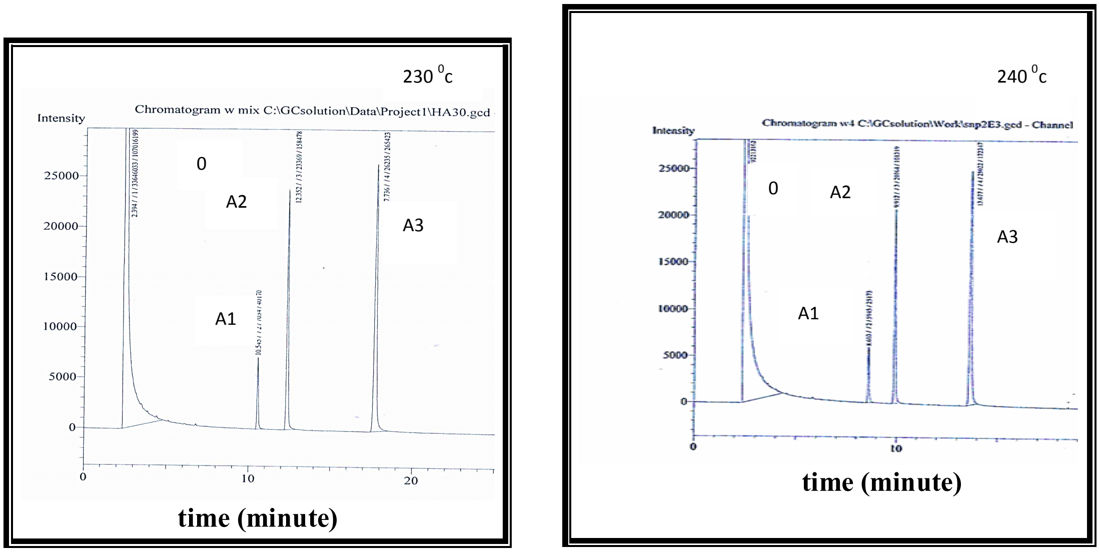


Fig (4): Separation of azo derivatives(A1,A2,A3) where solvent: ethanol(0) .Stationary phase: ZB -FFAP capillary column (30m ,0.25 mm I.D,0.25µm film thickness); injector temp 270C; total flow rate: 30 ml min -1, split ratio:1:50

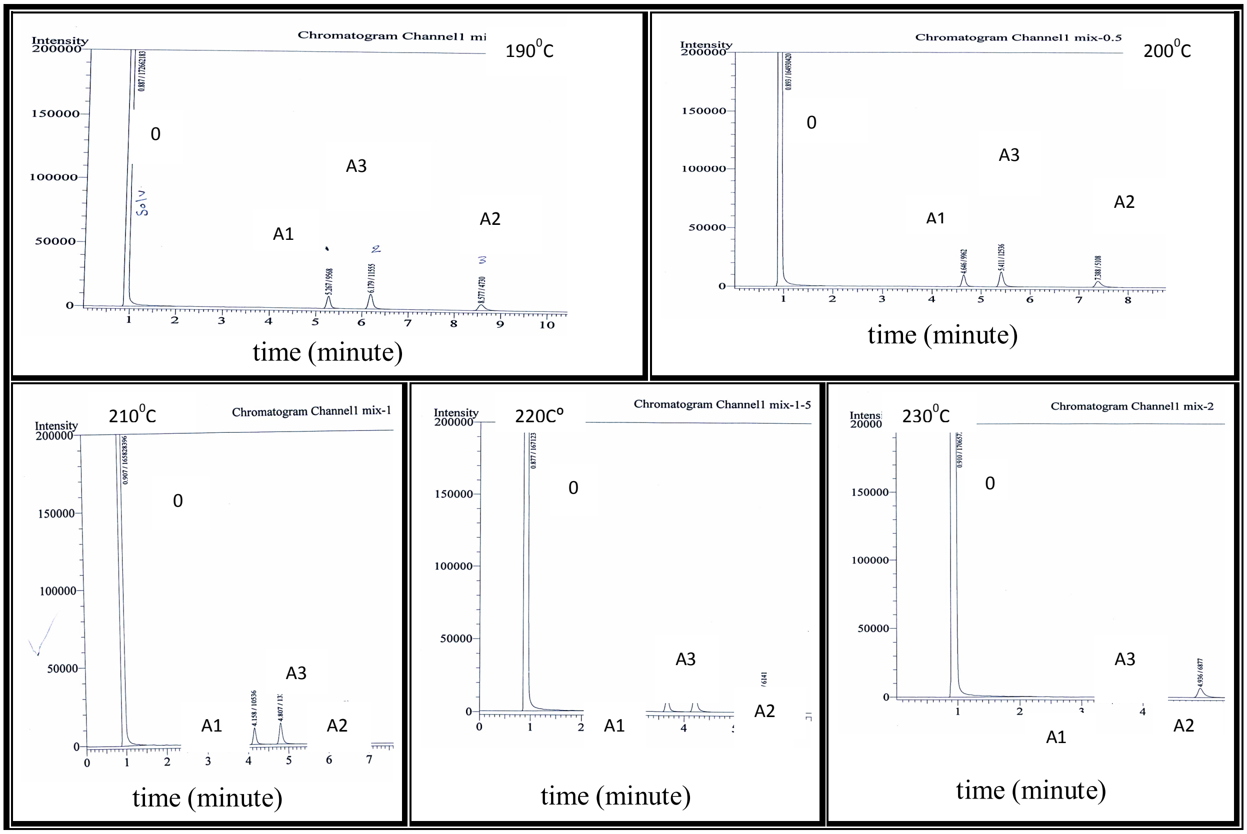


Fig (5): Separation of azo derivatives (A1, A2, A3) where solvent: ethanol (0) .Stationary phase: OV-5 capillary column (60m, 0.32 mm I.D, 0.25µm film thickness); injector temp.: 270^0C; total flow rate: 30 ml min -1, split ratio: 1:50.

The order of elution of the studied compounds were as follow: (A1) then(A2)then (A3) on the polar stationary phases fused silicaBP10, ZB-FFAT were mainly according to the interactions between p- cresol derivative and ZB-FFAT, BP10. But the orders of elution of the studied compounds were as follow: (A1) then (A3)then (A2)on thenon-polar stationary phase OV-5 follow the molecular weight due to the non-polar of OV-5.

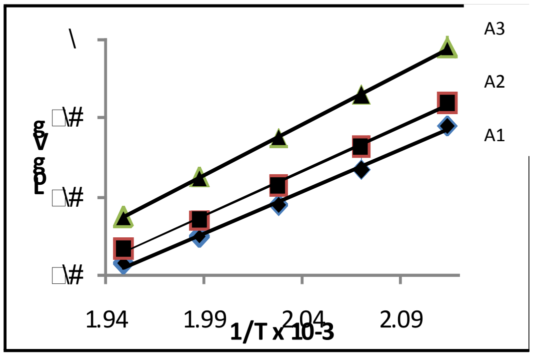


Fig (6): Plot of log Vg^0 vs. 1/T for organic Reagents onBP 10 at different column temp.

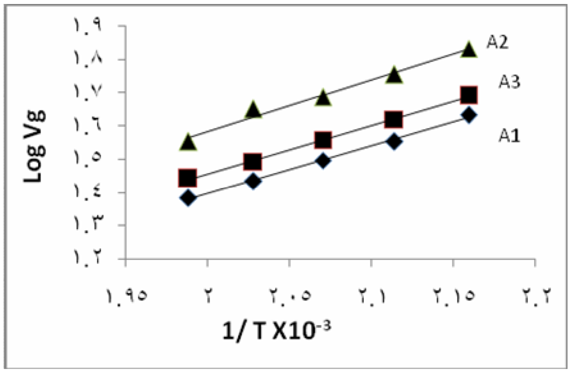


Fig (7): Plot of log Vg vs.1/T for organic Reagents on OV -5 at different column temp.

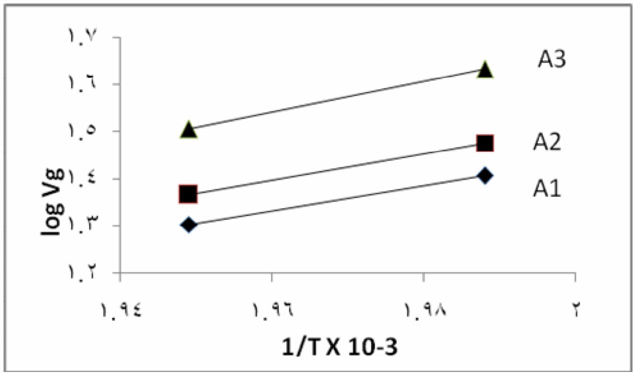


Fig (8):Plot of log Vg^0 vs. 1/T for organic reagents on ZB –FFATat different column temp.

Table 3: Thermodynamic data of A1, A2 and A3 onBP10

Comp No.	ΔS^0	ΔH^0	ΔG
A1	-2.602	-39.472	1295.354
A2	-2.946	-43.199	1468.099
A3	-3.515	-49.660	1753.535

Table 4: Thermodynamic data of A1, A2and A3 on OV-5

Comp No.	ΔS^0	ΔH^0	ΔG
A1	-1.484	-27.525	718.927
A2	-1.524	-29.704	736.868
A3	-1.484	-28.100	718.352

Table 5:Thermodynamic data of A1,A2 and A3 on ZB-FFAT

Comp No	ΔS^0	ΔH^0	ΔG
A1	-3.894	-50.960	1946.662
A2	-4.182	-54.401	2090.965
A3	-4.891	-62.735	2446.707

Table 6:Chromatographic parameters for A1,A2andA3

Liquid phase	R_S	N	HETP	Degree
BP(10)	1.46	4678.992	6.411×10^{-3}	210^0C
Z-B (FFA)	1.42	12010.793	2.497×10^{-3}	230^0C
OV-5	1.55	1914.552	0.031	200^0C

Conclusions

From figures (6-8) were produced a linear relationship between whole p-cresol derivatives and used stationary liquid phases due to normal chromatographic behavior for all compounds. Negative ΔH value describe more affection between azo derivatives compounds and stationary phases, which is indicate that more negative and lead to increasing of interaction (16), therefore tables (3-5) were observed that (ZB-FFAT) high polarity column causes increase of negative value of ΔH which is more interaction with studied compounds. On other hand the more negatively on ΔS means high irregularity on separation column.Table (6) shows that BP-10 the best column was appear high separation value, so it was the optimum separation efficiency for p-cresol derivatives through temperature range (200-240)^{0}C.

References

1 Sharples W.E;Dev., ***Chromatograph***., 1978, **1,** 87-116.

2 John V., ***Hinshaw***; 2001, LCGC**6,** 1056.

3 Antoaneta E., Oleg B.,Alina S. and Thomas S., ***Microchemical Journal***, 2012, **100,** 36–41

4 S.M. Bamforth, I. Singleton; ***J. Chem. Technol.biotechnology***, 2005, **80,** 723–736.

5 C.R. Estrellan, F. Iino; ***Chemosphere***, 2010, **80,** 193–207.

6 A.J. Britten, K.P. Naikwadi; ***J. Environ. Anal. Chem.***, 2009, **89 (15),** 1113–1123.

7 Robert C. Kong, Steven M. Fields, W.Paul Jackson, Milton L. Lee., ***Journal of Chromatography*** , 1984, **27,** 105–116

8 H.P. Ho, R.J. Lee, M.R. Lee, ***J. Chromatogr.***, 2008, **A 1213,** 245–248

9 L.W. Chung, M.R. Lee, ***Talanta***, 2008,**76**, 154–160.

10 Hans-Georg S., Sebastian G. , Stefan K. , UriF. , Carmen R. ,Julian K., Theodoros P. , Maria K., ***Journal***

of Chromatography, 2010, **1217,** 6769–6777

11 Marlin D.F., LillianG., Jean-Claude B., Fred. , ***DongxiangL.Environmental Health Perspectives***, 1993, **99**, 179-181.

12 Ryan B. Wilson. Christopher Siegler, Jamin C. Hoggard, Brian D. Fitz, Jeremy S. NadeauRobert E. Synovec , ***Journal of Chromatography A***, 2011, **1218,** 3130–3139

13 KadiMölder, Allan Künnapas, KoitHerodes, Ivo Leito; ***Journal of Chromatography*** **,** 2007**, 1160,** 227-234

14 Xueheng Z., Yiping L., Dennis. Phillips H.-Min Hwang a, Ian R. Hardin; ***Journal of Chromatography A***, 2007, **1159,** 217–224.

15 M.Gaber ,A.M.Hassanein and A.A.Lotfalla; ***J.of .Molecular Structure*** , 2008, **875,** 322-328.

16 N. Petsev and Chr. Dimitrov; ***J. Chromatog.***, 1966, **23**, 382.