



## ANALYSIS OF P-CRESOL DERIVATIVES BY GAS CHROMATOGRAPHY

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**Abstract-** The present study deals with the effect of temperature on the gas chromatographic behavior of some prepared P-cresol derivatives of azo dyes (4-MePAMP), (4-CPAMP), (4-OMePAMP), and (4-NPAMP) on fused silica (BP10), zebron (FFAT), and polysiloxane (OV-5) liquid stationary phases. The temperature increase is 10°C depend on maximum operation temperature (MOT) of columns. In general, the researchers found that the specific retention volume ( $v_g^0$ ) of p-cresol derivative compounds decreases by the increase of temperature of liquid stationary phases. The authors demonstrate thermodynamic data and calculate the separation factor ( $R_s$ ), number of theoretical plate (N), and highest equivalent of one theoretical plate (HETP) respectively.

**Keywords-** gas chromatography, p-cresol derivatives, separation, liquid stationary phases, Temperature

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### Introduction

In general, the gas chromatography method is the ability to separate and quantitatively determine mixture of organic substances. The separation mechanism depends on the stationary phase, rate of carrier gas, temperature, and column loading [1,2]. Gas chromatography-mass spectrometry was used for the determination of 16 priority polycyclic aromatic hydrocarbons (PAHs) [3]. In addition, it uses azo compounds that are free radical and its effects that these free radical generators have on commercially available stationary phases are described. Characteristics of the stationary phases are chain length, functional groups, and their roles in the cross [4-6]. A new micro extraction technique with gas chromatography-mass spectrometry was developed for determining of trace chlorophenols (CPs) in landfill leach ate [7]. In several publications chromatograms two peaks for azo-dyes such as Sudans, are observed. The origin of the "fast peak" is described as a "minor isomer of Sudan" in only one publication [8-10].

### Materials and Methods

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 8400 using KBr discs, Melting point were determined in open capillaries on Thomas Hoover apparatus 9300 -U.K., Micro analytical unit 1108 C.H.N elemental analyzer and Shimadzu GC-2014 gas chromatography equipped with flame ionization detector (F.I.D).

### Columns

The first column was 30m×0.25 mm I.D. ×0.25 μm film thickness zebron (FFAT), the second column was 30m×0.25mm I.D.×0.25μm film thickness fused silica (BP10), and the third column was 60m×0.32mm I.D×0.25μm film thickness polysiloxane (OV-5). The detail characteristics of liquid phases are listed in [Table-1].

Table 1- Characteristics of the used Liquid Stationary Phases

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

### Experimental Procedure

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

The titled azo derivatives from p- cresol were prepared according to literatures [11]. A solution of 2.1g of p-toluidine, 1.302 g of p-chloro aniline, 1.289 g of p-anisidine, and 1.315g of p-nitroaniline respectively in 5 ml of conc. HCl were added to a solution of 1.4 g of NaNO<sub>2</sub> dissolved in 25ml of water with stirring and cooling. This mixture is called dizonium salt (A) which is added to a solution of 4.18 ml of p-cresol with 3 g of NaOH with cooling. It is called coupling component (B). The mixture of (A) and (B) produce resultant

chromatic dyes which are washed by water, dried, and purified by recrystallization of ethanol. The properties and FTIR spectra data of compounds are listed in [Table-2].

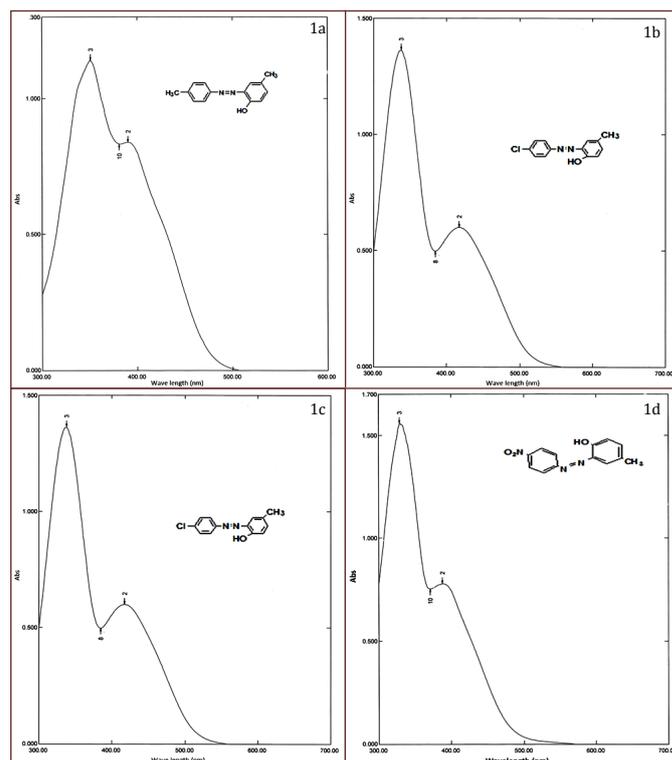
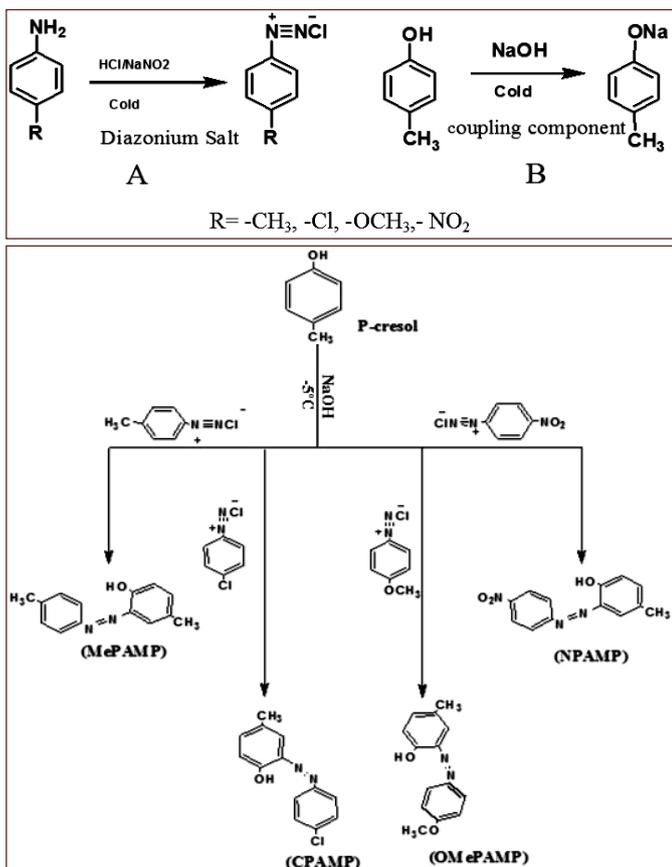


Fig. 1- UV-Vis Spectrum for organic reagents in ethanol solvent.

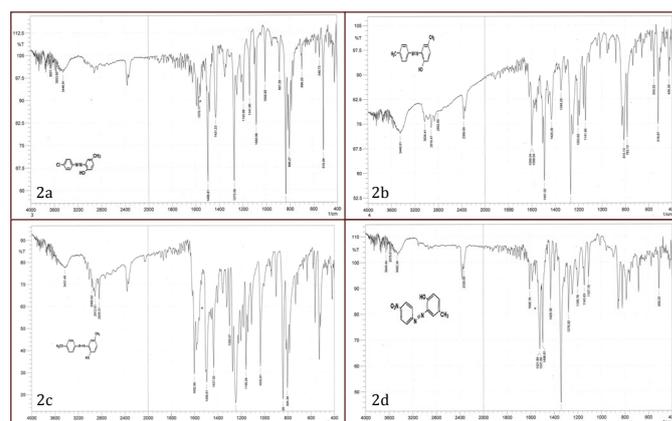


Fig. 2- FTIR spectra for organic reagents

### Studying the Effect of Temperature on the Chromatographic Behaviour

Mixtures were prepared by weighing 0.3 g of each compound and each one was blended in the glass cell. From mixture (0.1-0.6)  $\mu$ L were injected by 10  $\mu$ L Hamilton Syringe. The components of each mixture were run individually to determine the order of elution of these components. The analysis of each mixture was repeated twice and the reproducibility was with  $\pm 1$  percent. All the optimum conditions were kept throughout isothermal column temperatures ranged from (200-240) $^{\circ}$ C for F.S (BP10), (210-240) $^{\circ}$ C for ZB (FFAT), and (190-230) $^{\circ}$ C for OV-5.

### Results and Discussion

#### Spectrophotometric Studies

The first part of this study includes preparation four organic reagents which are derivatives from P-cresol. Identification of these compounds were done by UV-VIS and IR spectra are shown in [Fig-1] [Fig-2] respectively. The researchers found matching between the theoretical calculation and experimental figures with a way to suggest the final structures of the synthesized reagents by C.H.N analysis as it is demonstrated by [Table-2].

The prepared reagents are:

- 2[(4-methyl phenyl) azo]-4-methyl phenol (MePAMP).
- 2[(4-chloro phenyl) azo]-4-methyl phenol (CPAMP).
- 2[(4-methoxy phenyl) azo]-4-methyl phenol (OMePAMP).
- 2[(4-Nitro phenyl) azo]-4-methyl phenol (NPAMP).

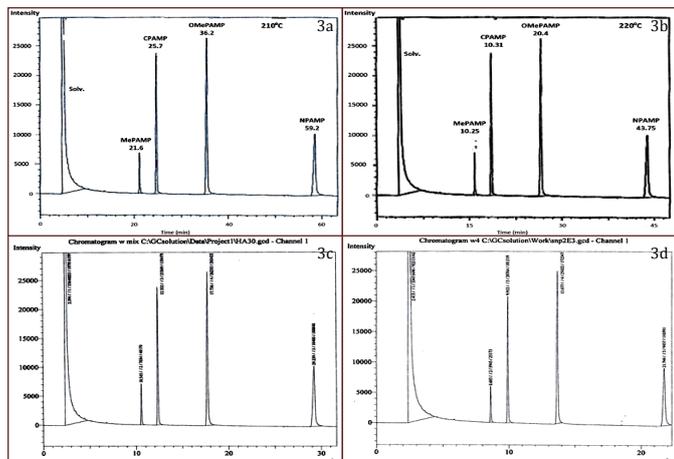
Table 2- Results of elemental analysis and some physical properties of organic reagents

Compound	M. Wt.	Yield(%)	M.P( $^{\circ}$ C)	Color	R <sub>f</sub>	Found (calc.) %		
						C	H	N
MePAMP	226.27	75	103	Orange	0.91	74.31	6.24	12.38
						74.54	6.06	12.05
CPAMP	246.06	70	154	Yellow	0.82	63.29	4.49	11.36
						64.06	4.29	11.64
OMePAMP	242.27	80	95	Red brown	0.85	69.41	5.82	11.56
						70.01	5.75	11.91
NPAMP	257.24	85	187	Deep Yellow	0.87	60.7	4.31	16.33
						60.62	4.4	16.3

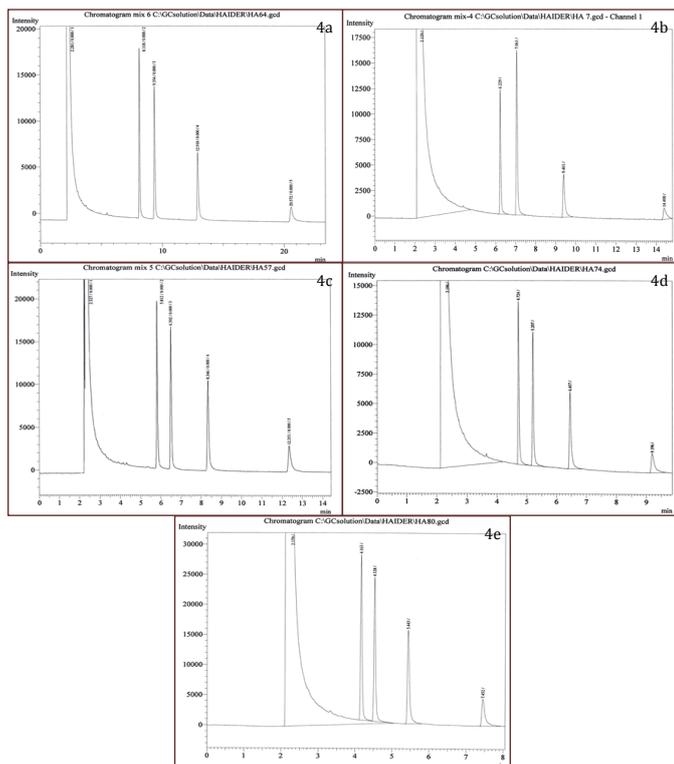
[Fig-3] shows that the order of elution of the studied compounds are: MePAMP, CPAMP, OMePAMP and finally NPAM. The nature of substitution groups (-CH<sub>3</sub>, -Cl, -OCH<sub>3</sub>, -NO<sub>2</sub>) of these compounds and its interaction with zebron (FFAT) as liquid stationary phase.

[Fig-4] represents the order of elution of the studies compounds on fused silica (BP-10) column are MePAMP, CPAMP, OMePAMP and

NPAMP. Our results have been showed the polarity of liquid stationary phase (BP-10) lead to increase of dipole-dipole interaction with azo compounds then increase of specific retention volumes.



**Fig. 3-** Separation of azo derivatives; solvent: ethanol, Stationary phase: ZB -FFAP capillary column (30m, 0.25 mm I.D, 0.25µm film thickness), injector temp 27°C, flow rate: 30 ml/ min, split ratio: 1:50

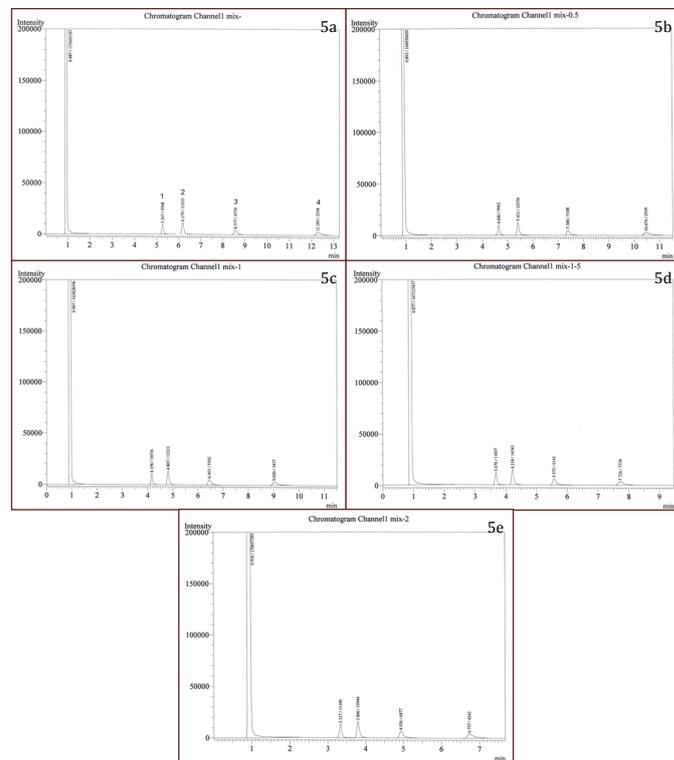


**Fig. 4-** Separation of azo derivatives; solvent: ethanol,. Stationary phase: fused-silica (BP10) capillary column (30m 0.25 mm I.D), injector temp.: 27°C, flow rate: 30ml min<sup>-1</sup>, split ratio: 1/50.

[Fig-5] reveals the chromatographic behavior of elution order and resolution of studies organic reagents on polysiloxane (OV-10) are MePAMP, CPAMP, OMePAMP and NPAMP at different column temperatures ranged from 200°C to 240°C at 10°C increment. The order of elution were related to molecular mass of prepared compounds that trend return to non-polar polysiloxane (OV-5) liquid stationary phase.

The order of elution of the studied compounds were as follow: (MePAMP), (CPAMP), (OMePAMP), and (NPAMP) on the polar

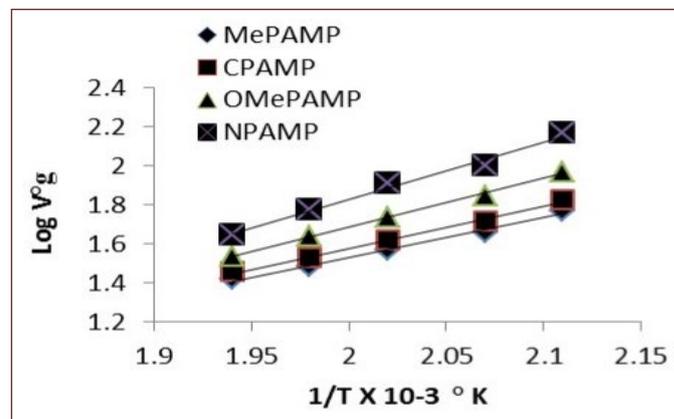
stationary phases which are BP10 and ZB-FFAT that are mainly interacted with p- cresol derivative, but the orders of elution of the studied compounds were as follow: ((MePAMP), (CPAMP), (OMePAMP), and (NPAMP) on stationary phase OV-5 due to their molecular weight on the non-polar of OV-5.



**Fig. 5-** Separation of azo derivatives; solvent: ethanol, Stationary phase: OV-5 capillary column (60m, 0.32mm I.D, 0.25µm film thickness), injector temp.: 270°C, flow rate: 30ml min<sup>-1</sup> and split ratio: 1:50.

**Conclusions**

[Fig-6], [Fig-7] and [Fig-8] shows a linear relationship between whole p- cresol derivatives and used stationary liquid phases due to normal chromatographic behavior for all compounds. Negative ΔH value describes more affection between azo derivatives compounds and stationary phases, which is indicate that more negative and lead to increasing of interaction [12], therefore [Table-3], [Table-4] and [Table-5] were observed that (ZB-FFAT) high polarity column causes increase of negative value of ΔH which has more interaction with studied compounds.



**Fig. 6-** Plot of log Vg° vs. 1/T of organic

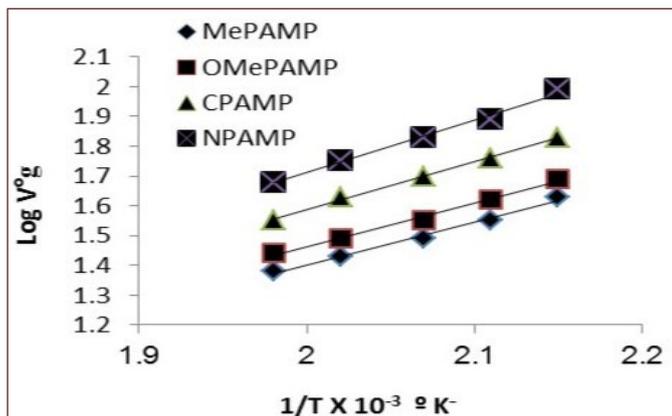


Fig. 7- Plot of log Vg° vs. 1/T of organic reagents on BP 10 at different column temp. reagents on OV -5 at different column temp.

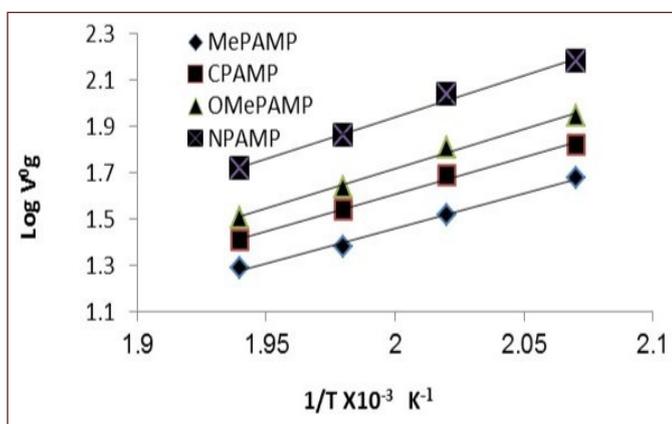


Fig. 8- Plot of log Vg° vs. 1/T of organic reagents on ZB - FFAT at different column temp

Table 3- Thermodynamic data of organic reagents on ZB-FFAT

No.	Compounds	$\Delta S^\circ$ KJ.mol <sup>-1</sup>	$\Delta H^\circ$ KJ.mol <sup>-1</sup>	( $G\Delta$ ) KJ.mol <sup>-1</sup>
1	MePAMP	-4.64	-13.95	2319.97
2	CPAMP	-4.78	-14.6 2	2389.72
3	OMePAMP	-5.18	-15.79	2599.75
4	NPAMP	-5.28	-16.52	2639.32

Table 4- Thermodynamic data of organic reagents on BP10

No.	Compounds	$\Delta S^\circ$ KJ.mol <sup>-1</sup>	$\Delta H^\circ$ KJ.mol <sup>-1</sup>	( $G\Delta$ ) KJ.mol <sup>-1</sup>
1	MePAMP	-2.6	-9.42	1246.38
2	CPAMP	-2.94	-10.34	1409.68
3	OMePAMP	-3.51	-11.85	1683.48
4	NPAMP	-4.14	-13.63	1985.99

Table 5- Thermodynamic data of organic reagents on OV-5

No.	Compounds	$\Delta S^\circ$ KJ.mol <sup>-1</sup>	$\Delta H^\circ$ KJ.mol <sup>-1</sup>	( $G\Delta$ ) KJ.mol <sup>-1</sup>
1	MePAMP	-1.47	-6.54	394.77
2	OMePAMP	-1.46	-6.68	683.9
3	CPAMP	-1.61	-7.32	754.21
4	NPAMP	-1.81	-8.05	848.08

Table 6- Chromatographic parameters of organic reagents

No.	Liquid phases	RS	N	HETP	T (°C)
1	(ZB -FFA)	1.42	12010.79	2.497×10 <sup>-3</sup>	230°C
2	(BP-10)	1.5	4678.992	6.411×10 <sup>-3</sup>	210°C
3	(OV-5)	1.55	1914.552	31×10 <sup>-3</sup>	200°C

On other hand, the more negatively on  $\Delta S$ , the high irregularity on separation column. [Table-6] shows that BP-10 was the best column that appears high separation value, so it was the optimum

separation efficiency for p-cresol derivatives through temperature range (200-240)°C.

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