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Temperature Effect on the Chromatographic Behavior of Some Organophosphorus Compounds on LAC-Series as Stationary Phases

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Abstract:

This study deals with the chromatographic behavior that is order of elution and resolution of some organophosphorus compounds [Dimethyl phosphate (DMPH), Dimethyl methyl phosphate (DMMP), Tri methyl phosphate (TMPO), Triethyl phosphate (TEP).] on various polyesters liquid phases LAC-series [Poly ethylene glycol succinate (LAC-886), Poly diethylene glycol succinate (LAC-738), Poly ethylene glycol tetrachlorophthalate (LAC-772), Poly diethylene glycol adipate (LAC-296), and poly neopentyl glycol adipate (LAC-769).] by using flame ionization detector (FID)in gas chromatography at different column temperatures ranged from 90Cº to 180Cº at 10Cº increasment. On optimum carrier gas (nitrogen) flow rate of 30 ml min^{-1} . Detector temperature and column inlet temperature were set above of column temperature (50) Cº, (25) Cº respectively.

Aim: To find the optimum conditions to separate organophosphorus compounds in various polyesters liquid phases.

Introduction:

In gas-liquid chromatography, the choice of conditions for any separation involves balancing a number of conflicting factors such as temperature, rate of carrier gas, length of column [(1)] columns loading and the selectivity of the liquid phase [(2)].

A direct solvent extraction-gas chromatographic method was developed for the determination of organophosphorus compounds as additives in lubricating oil for control purposes. Ethanol (95%) was used as an extracted and Varian GC-Vista 6000 gas chromatography with a 3% OV-17 column and dual flame photometric detector was used for the measurements under the optimum experimental conditions. The accuracy and precision of the method were determined by preparing model samples of different types of engine lubricating base oils blended with different amounts of triphenyl phosphate or p-tricresyl phosphate ranging from 0.002 to 1.0% (w/w), which correspond to 2.12-955 ppm of phosphorus[(3)].

A method for the simultaneous determination of 10 pesticides (organochlorines, organophosphorus compounds with atomic emission detection (GC-AED) is reported. Soil samples are first "cleaned –up" with 25ml of an ascorbic acid solution (pH 2.15).

The aqueous phase is extracted with ethyl acetate, and the solid residue is then extracted twice with 10ml of ethyl acetate [4].

A miniaturized flame photometric detector has been constructed and interfaced to an ultra fast GC system for the specific detection of organophosphorus and organo-sulfer compounds. It could lead to a portable system for real-time [5].

Zaidan study the effect of temperature on the gas-chromatographic behavior of organophosphorus compounds (DMPH, DMMP, $MPSCl_2$, TMP, TMPO, TEP) with dimethyl polysiloxane liquid stationary phase OV-101 and polyester LAC-860 liquid stationary phase. This study shows that there is abnormal chromatographic behavior for these compounds on LAC-860 liquid stationary phase comparing with the normal chromatographic behavior of the same compounds on OV-101 liquid stationary phase [6].

Experimental:

Apparatus:

A Beckman GC-45: gas chromatography equipped with a flame ionization detector was used with on optimum carrier gas (nitrogen) flow rate of 30 ml min^{-1}.

Recording was done on a Beckman model 10. Columns were made of stainless steel tubing (182.9cm long, 6.35mm O.D and 4mm I.D.).They were packed with 20% by weight of different liquid stationary phases on chromosorb W (80-100) mesh.

Materials and Solutions:

All compound used in this work obtained from Fluka AG, and BDH chemical Ltd., no further purification was needed.

Sampling:

Samples were prepared individually by dissolving 10ML of each compound (DMPH, DMMP, TMPO, and TEP) in 1ml chloroform. Mixture was prepared by mixing 100ML from each of prepared solution. Sample sizes ranged from (0.1-0.6) ML, the injection were made with a (1.0) ML Hamilton syring.

Result and Discussion:

Elution and resolution of organophosphorus compounds on polyesters liquid stationary phases.

LAC-886: Table (1), Fig. (1)

The order of elution of the studied compounds was as follow:

TMPO < DMMP < DMPH < TEP

At(Fig.1) an abnormal chromatographic behavior was observed at the temperature range (100-110) C^o that is at 110 C^o an abrupt increase in specific retention volumes was recorded. And the plot of log Vg^o verses 1/T was no longer linear. Further more at the temperatures range (120-140) C^o a noticeable improvement in resolution was observed then as temperature increases no separation was obtained, especially at 180 C^o (Fig.1).

LAC-738: Table (2), Fig. (2)

The Vg^o values of these compounds on this liquid phase were in the following order:

DMMP < TEP < TMPO < DMPH

The specific retention volumes of the studied compounds on LAC-738 were generally higher than on LAC-886. The increase in polarity of liquid phases would cause more dipole-dipole and dipole induced dipole interactions between the liquid phase and the organophosphorus compounds, and the leads to an increase in the Vg^o values [7, 8].

At the temperature range (130-140) C^o a noticeable improvements in resolution was observed.

LAC-772: Table (3), Fig. (3)

The order of elution was a follow:

TMPO < TEP < DMMP < DMPH

And the separation efficiency on this liquid phase was very low probably because of six electrons with drawing groups attached to the phenyl ring, so this decreases the polarizability of stationary liquid phase.

LAC-296: Table (4), Fig. (4)

The Vg^o values of these studied compounds on this liquid stationary phase were in the following order:

DMMP < TMPO < TEP < DMPH

Good resolution was observed at the temperature range (130-140) Cº with an increase in specific retention volumes.

LAC-769: Table (5), Fig. (5)

The chromatographic behavior of organophosphorus compounds on LAC-769 liquid phase was similar to LAC-296, that is an increase of temperatures to certain value on (critical temperature) leads to increase of resolution of there compounds.

Generally these series of liquid phases (LAC-series) showed an abnormal chromatographic behavior towards organophosphorous compounds that is an increase in specific retention volumes or improvements in separation or both at certain column temperatures (critical temperatures), the values of these critical temperatures varied according to the structure of liquid stationary phase.

Some researchers found the same behavior when these liquid stationary phases were used further separation of thiophenes, furans, thioles, alkanes, aldehydes, ketones, pyridines and anilines [9-15].

Differential thermal analysis (DTA) [16] revealed the existence of some structural rearrangements at these critical temperatures.

In this investigation, thermodynamic parameters were calculated for organophosphorus compounds on some of polyesters liquid phases; in which the partial molar enthalpy ΔHs^{o} of solutions were calculated from the slope of the linear relation of Log Vg^{o} vs. 1/T table(6). There are values of ΔHs^{o}, which means the highest interaction between LAC-296 and these compounds [17].

Table (1): Specific retention volume (Vg^{o}) ml/gm of organophosphorus compounds dissolved in chloroform on (LAC-886) stationary liquid phase at different column temperatures.

Compound	90Cº	100Cº	110Cº	120Cº	130Cº	140Cº	150Cº	160Cº	170Cº	180Cº
DMPH	202.76	134.55	154.94	100.08	76.98	52.13	39.21	38.25	34.58	25.90
DMMP	287.66	206.47	218.26	142.69	108.73	72.84	50.94	49.56	38.89	34.02
TMPO	349.65	259.70	289.08	184.86	140.72	86.69	62.91	60.87	48.17	37.97
TEP	184.02	135.40	167.41	119.60	94.44	60.62	46.90	44.39	35.69	27.43

Table (2): Specific retention volume (Vg^o) ml/gm of organophosphorus compounds dissolved in chloroform on (LAC-738) stationary liquid phase at different column temperatures.

Compound	90C°	100C°	110C°	120C°	130C°	140C°	150C°	160C°	170C°	180C°
DMPH	580.07	415.55	284.90	193.64	137.41	130.96	83.84	72.21	86.90	68.05
DMMP	1382.87	900.31	667.84	417.27	270.82	255.30	119.91	57.05	84.52	65.21
TMPO	857.48	742.83	593.83	378.71	243.57	217.83	139.73	71.55	80.55	63.01
TEP	1238.16	827.68	599.57	419.86	309.26	290.27	165.21	85.74	85.69	65.68

Table (3): Specific retention volume (Vg^o) ml/gm of organophosphorus compounds dissolved in chloroform on (LAC-772) stationary liquid phase at different column temperatures.

Compound	90C°	100C°	110C°	120C°	130C°	140C°	150C°	160C°	170C°	180C°
DMPH	-----	-----	127.35	89.74	60.95	43.95	38.19	25.12	21.53	19.63
DMMP	-----	-----	187.07	124.16	91.83	70.47	53.09	37.49	25.94	23.07
TMPO	-----	-----	216.77	148.25	109.65	78.34	57.94	40.74	34.75	24.38
TEP	-----	-----	197.24	127.94	92.89	70.80	53.58	37.32	32.66	24.38

Table (4): Specific retention volume (Vg^o) ml/gm of organophosphorus compounds dissolved in chloroform on (LAC-296) stationary liquid phase at different column temperatures.

Compound	90C°	100C°	110C°	120C°	130C°	140C°	150C°	160C°	170C°	180C°
DMPH	687.19	469.18	274.11	177.56	125.37	89.61	84.23	72.94	66.63	52.62
DMMP	1743.04	1264.70	690.72	430.88	278.61	189.28	102.76	84.49	59.32	51.63
TMPO	3054.49	991.48	547.67	346.62	228.74	156.74	90.63	70.94	54.16	41.44
TEP	1151.10	641.54	391.38	250.67	163.46	123.86	107.98	88.34	66.96	52.95

Table (5): Specific retention volume (Vg^o) ml/gm of organophosphorus compounds dissolved in chloroform on (LAC-769) stationary liquid phase at different column temperatures.

Compound	90C°	100C°	110C°	120C°	130C°	140C°	150C°	160C°	170C°	180C°
DMPH	333.54	227.83	153.56	110.85	79.65	63.58	54.40	42.12	36.37	25.99
DMMP	851.58	565.08	358.48	237.23	154.91	111.48	79.61	56.95	46.41	34.89
TMPO	808.73	525.50	346.80	156.36	122.41	107.77	87.17	63.59	46.30	33.58
TEP	801.42	450.78	294.57	195.93	134.28	106.29	84.12	73.34	52.14	35.90

Table (6): Partial molar enthalpy of solution (ΔHs^o) K.Cal/mol. of organophosphorus compounds on different (LAC-series) liquid stationary phases

Compound	LAC-772	LAC-296	LAC-769
DMPH	10.24	10.55	8.29
DMMP	9.56	12.06	10.83
TMPO	8.53	11.73	10.47
TEP	8.91	10.84	9.57

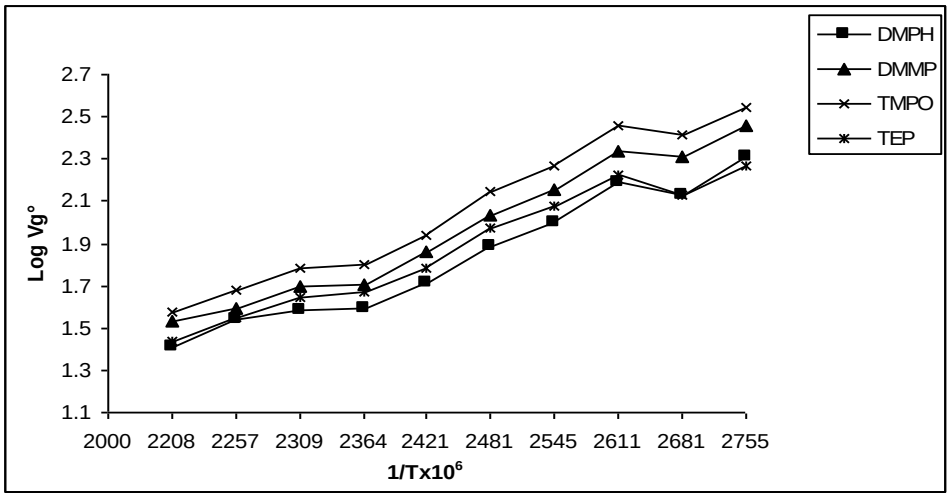

Fig. (1): Plots of the logarithm of the specific retention volumes for the studied compounds against the reciprocal of absolute column temperature on (LAC-886)

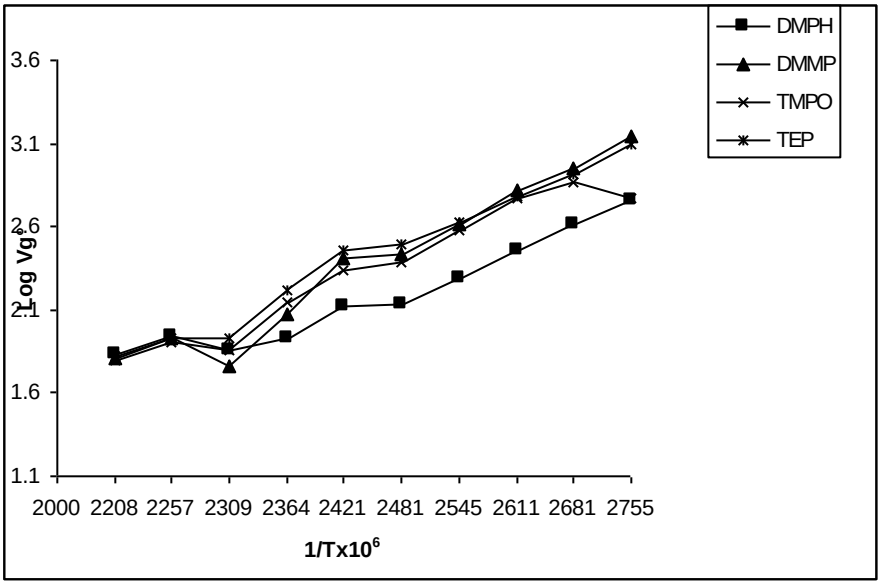

Fig. (2): Plots of the logarithm of the specific retention volumes for the studied compounds against the reciprocal of absolute column temperature on (LAC-738).

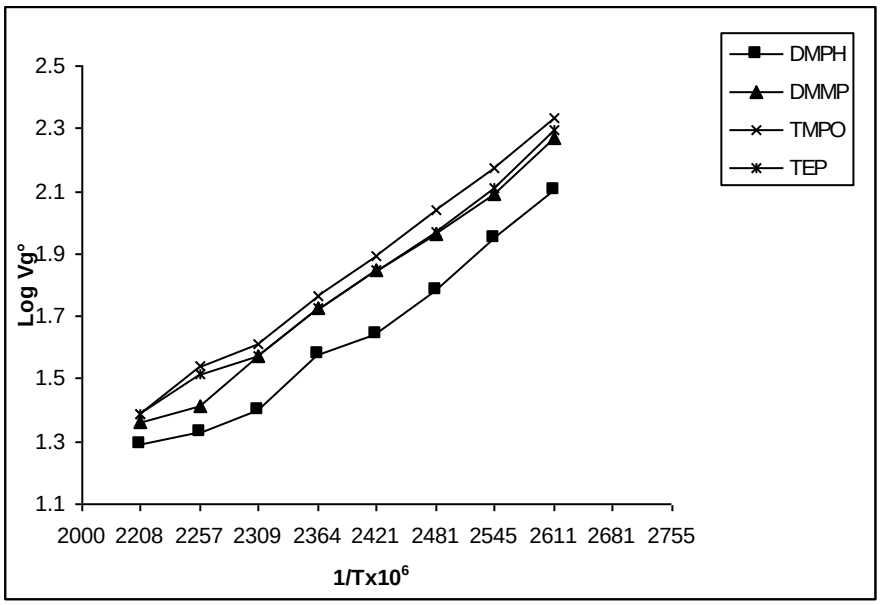

Fig. (3): Plots of the logarithm of the specific retention volumes for the studied compounds against the reciprocal of absolute column temperature on (LAC-772).

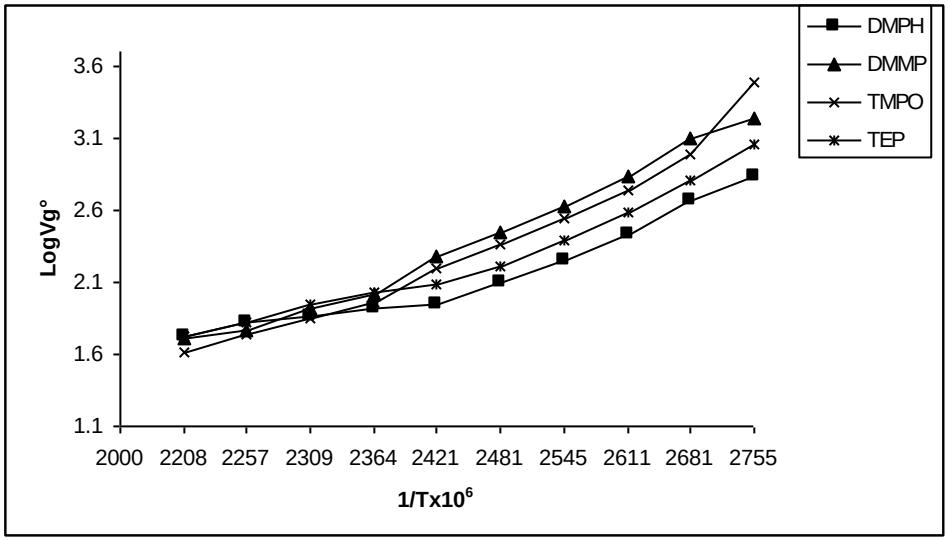

Fig. (4): Plots of the logarithm of the specific retention volumes for the studied compounds against the reciprocal of absolute column temperature on (LAC-296)

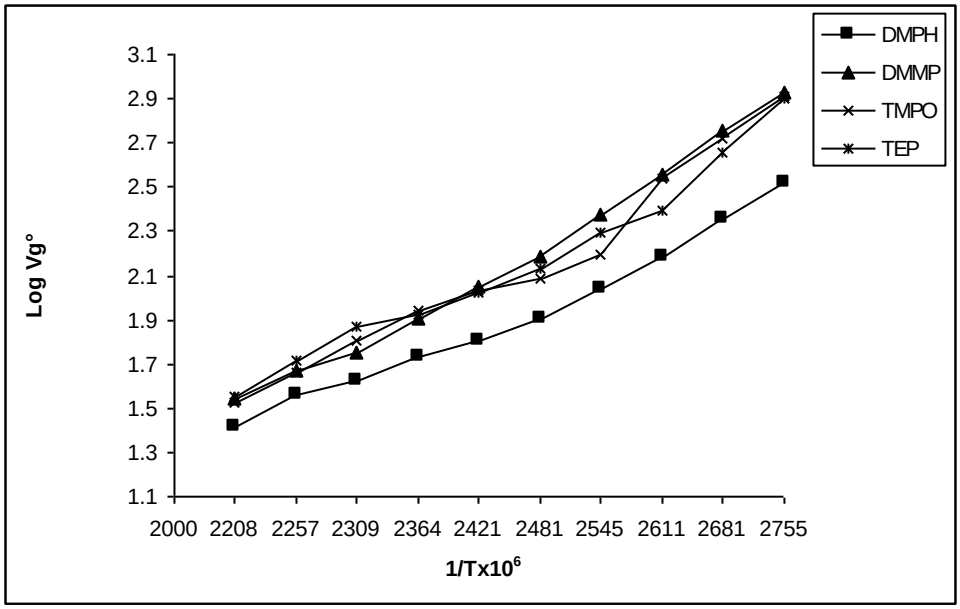

Fig. (5): Plots of the logarithm of the specific retention volumes for the studied compounds against the reciprocal of absolute column temperature on (LAC-769).

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التأثير الحراري على التصرف الكروماتوغرافي لبعض مركبات الفسغور العضوية على الأطوار السائلة الثابتة متعدد الاسترات

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الخلاصة:

تم في هذا البحث دراسة السلوك الكروماتوغرافي لمركبات الفسفور العضوية [(ثنائي مثيل فوسفيت (DMPH) ، ثنائي مثيل مثيل فوسفات (DMMP) ، ثلاثي مثيل فوسفات(TMPO) ، ثلاثي أثيل فوسفيت (TEP)] . على الأطوار السائلة الثابتة من نوع متعدد الاسترات المختلفة [سكسينات كلايكول الايثيلين (LAC-886) ، سكسينات كلايكول ثنائي الايثيلين (LAC-738) ، رابع كلورات فثاليت أثيلين كلايكول (LAC-772) ، أديبات كلايكول ثنائي الاثيلين (LAC-296) ، أديبات كلايكول نيوبنتان (LAC-769)] . وقد أستخدم مجس التأين أللهبي (FID) المثبت في جهاز (Beckman GC-45) لدراسة المركبات الأربعة في مدى درجات حرارة عمود يتراوح بين (90-180) م^{o} ، وكان مقدار الزيادة التدريجية في درجة حرارة العمود (10) م^{o} ،وقد أستخدم غاز النيتروجين كغاز ناقل وبسرعة حجميه مثلى (30) سم^{3} دقيقة$^{-1}$. أما درجة حرارة المجس ومدخل العمود فكانت أعلى من حرارة العمود (50) م^{o} و (25) م^{o} على التوالي.