CBP-5

Effect of changing air to hydrogen ratio on the performance of flame photometric detector (S-mode) in the analysis of Organophosphorus – Pesticides by GC-FPD

A.Y. Kilany*, M. A. Elsayed *, M. K. Abd ElMegid*

Abstract

In the present work, a sensitive method for the quantification of Organophosphorus – Pesticides (Malathion and Dimethoate) has been improved. The performance of flame photometric detector (FPD) was evaluated in terms of sensitivity, selectivity and reproducibility. The detector was strongly depending on the absolute and relative flow rates of air and hydrogen gases. The best air-to-fuel ratio for both Malathion and Dimethoate was found to be 0.6 (S mode), the minimum detection limit was found to be 0.0135 mg/l and wide linear dynamic range from 0.04038 to 1212 mg/l.

Keywords:
Detector sensitivity, Minimum detectability, dynamic Range, linear Range, malathion, dimethoate, organophosphorus pesticides, , GC/FPD.

Egyptian Armed force

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

**8ᵗʰ International Conference
on
Chemical & Environmental
Engineering**
19 – 21 April 2016

1- Introduction

Organophosphorus (OP) pesticides are widely used in agriculture as insecticides due to their high activity, low bioaccumulation and moderately rapid degradation in the environment.
The measurements of OP compounds are classically done using chromatographic techniques,[1-6]. Malathion S-[1, 2-di (ethoxycarbonyl) ethyl] dimethyl phosphoro-thiolothionate and Dimethoate is (O,O-dimethyl S-methyl-carbamoyl-methyl phosphorodithioate.) Dithiophosphate is a member of a general class of organophosphorus or organophosphate (OP) pesticides, [7, 8, 9, 10].
The FPD detects compounds by burning those compounds in a flame and sensing the increase of light emission from the flame during that combustion process. Therefore, the FPD is a flame optical emission detector comprised of a hydrogen-air flame, an optical window for viewing emissions generated in the flame, an optical filter for spectrally selecting the wavelengths of light detected, a photomultiplier tube for measuring the intensity of light emitted, and an electrometer for measuring the current output of the photomultiplier. The sensitivity and specificity of the FPD are strongly dependent on the absolute and relative flow rates of hydrogen and air. The optimum hydrogen and air flow rates depend on the detailed configuration of the flame burner. For some FPD designs, the flows which are optimum for phosphorus detection are not the same as the flows which are optimum for sulfur detection. Also, the flows which are optimum for one sample compound may not necessarily be optimum for another sample compound, [11].

2- Experimental
2.1- Reagents and solution

Malathion and Dimethoate were purchased from Nasr Company for intermediate chemicals; purity >95%. Stock standard solutions were prepared by accurately weighing 0.3 g of pure material. Malathion and Dimethoate was dissolved in pesticide-quality benzene and diluted to volume in a 25-mL volumetric flask. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Stock standard solutions were transferred into TFE-fluorocarbon-sealed screw-cap vials, stored at 4°C and protected from light. A set of test samples were Prepared by dilution from stock standard solutions covering a wide range of concentrations. A fixed volume (1μL) of each concentration of the test substance were injected, the height (H) and integrated peak area (A) of the resultant Gaussian or chromatographic peaks were measured. Frequently stock standard solutions were checked for signs of degradation or evaporation.

2.2- Apparatus

Agilent, 7890A gas chromatograph, Autosampler (7693-series) with a split/ Splitless injector system and a flame photometric detection with sulfur filter were used. Ultra pure nitrogen

(99.9999%) at 25 psi constant pressure was passed through a molecular sieve trap and an oxygen trap was used as the carrier gas. The injection port was held at 200 ^{0}C and used in the splitless mode. Separation was carried out on a HB-5, 30 m x 0.32 mm capillary column with a 0.25 µm stationary film thickness (Agilent Technologies). Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g. The column temperature was maintained at 60 ^{0}C for 1 min and then programmed at 20 ^{0}C /min to 250 ^{0}C, and held for 5 min. The total analysis time was 15.5 min. The volume of sample injected in splitless mode was 1.00 µL. Absolute and relative flow rate of air and hydrogen used for flame photometric detector were studied from 0.4-1.2 air-to-hydrogen ratio.

3- Results and Discussion

3.1 Effect of Air-to-Hydrogen Ratio On Detector Response (FPD-S-mode) With Malathion and Dimethoate

The effect of changing the air-to-hydrogen ratio from 0.4-to-1.2 in detector response has been studied with both malathion and dimethoate. The result of the detector response with malathion and dimethoate are shown in table 3.1 and 3.2 The optimum value for this ratio for malathion and dimethoate as shown in figure 3.1 and 3.2 is 0.6.

As shown from the figures, at ratios less than 0.5 the flame seems to have not enough energy to produce the desired optical emissions from S_2 molecular systems and the device give no signal. While at air to hydrogen ratio 0.6 the detector is reach to the maximum response this may be indicate to those regions of an FPD flame which are locally rich in H-atoms optical emissions from the S_2 molecular systems are highly favored and can be detected by FPD-S mode on the other hand at those regions of an FPD flame (larger than 0.6) which are locally rich in O-atoms optical emissions from CH and C_2 light emissions from hydrocarbons molecular systems are highly favored, that cannot be detected by the detector.

Table 3.1 Detector response (FPD-S-mode) with different air-to-H_2 ratio with Malathion

Ratio	Air ml/min	H_2 ml/min	Area count
1.2	60	50	4646.7
1	50	50	4293.6
0.8	40	50	3858.8
0.7	35	50	3153.8
0.6	30	50	25147374
0.5	25	50	No signal

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

**8th International Conference
on
Chemical & Environmental
Engineering**
19 – 21 April 2016

Table 3.2 Detector response (FPD-S-mode) with different air-to-H_2 ratio with Dimethoate

Ratio	Air (ml/min)	H_2 (ml/min)	Area count
1.2	60	50	3929.2
1	50	50	4389.8
0.8	40	50	3993.2
0.7	35	50	3769.8
0.6	30	50	23029318
0.5	25	50	No signal
0.4	20	50	

3.2 Effect of Total Gas Flow Rate Air + Hydrogen on Detector Response (FPD-S-mode) With Malathion and Dimethoate At Constant Air To Hydrogen Ratio

The effect of changing the total gas flow rate from 48 to 112 ml/min with air-to-H_2 ratio of 0.6 for both malathion and dimethoate on the detector response has been studied. Table 3.3 and 3.4 show the detector response with different total gas flow rates for malathion and dimethoate. Figure 3.3 and 3.4 show the relation between detector response with different gas flow rates with malathion and dimethoate by GC-FPD-S mode.

As indicated from the figures and tables, detector response increase as the total gas flow rate increase this may be indicated to the high energy generated from the flame, this energy increased as the total gas flow rate pass through the detector increased. As indicated from the recommendation for GC operating condition, the maximum flow rate of hydrogen 70 ml/min with S mode so we don't operate more hydrogen flow rate for more safety and to avoid explosion.

Table 3.3 Detector response at different gas flow rates during the analysis of malathion by GC-FPD-S-mode

Total gas flow rate at 0.6ratio	Air (ml/min)	H_2 (ml/min)	Area count
112	42	70	10922700
96	36	60	11472793
80	30	50	15291003
64	24	40	11588660
48	18	30	Flame out

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

**8ᵗʰ International Conference
on
Chemical & Environmental
Engineering**
19 – 21 April 2016

Table 3.4 Detector response at different gas flow rates during the analysis of dimethoate by GC-FPD-S-mode

Total gas flow rate at 0.6ratio	Air (ml/min)	H_2 (ml/min)	Area count
112	42	70	12461000
96	36	60	13780502
80	30	50	14386048
64	24	40	11588660
48	18	30	Flame out

The obtained result from studying these two factors (absolute and relative flow rates) with two materials (malathion and dimethoate) with FPD-S mode indicating that, by judicious gas flow rates (absolute and relative gas flow rate), for sulfur detection, light emanating from the S_2 molecule is generally detected. The important chemical species in hydrogen – air flame are the H, O, and OH flame radicals. These highly reactive species play a major role in decomposing incoming samples and in the subsequent production of the desired optical emissions. Optical emissions from the S_2 molecular systems are highly favored in those regions in FPD flame which are locally rich in H-atoms as shown with ratio 0.6 for both malathion and dimethoate, while CH and C_2 light emissions from hydrocarbons originate mainly from those flame regions which are locally rich in O-atoms as shown in the other ratios of the study. The highest sensitivity and specificity for sulfur and phosphorus detection are achieved only when the FPD flame is operated with hydrogen in excess of that stoichiometric amount required for complete combustion of the oxygen supplied to the flame. The optimum hydrogen and air flow rates depend on the detailed configuration of the flame burner. For some FPD designs, the flows which are optimum for phosphorus detection are not the same as the flows which are optimum for sulfur detection as shown from the present study. Also, the flows which are optimum for one sample compound may not necessarily be optimum for another sample compound such as with malathion and dimethoate [11,12].

3.3 Linearity of the Detector (FPD-S mode) with Malathion and Dimethoate

The linearity of the detector response to the analytes concentration (malathion and dimethoate) was determined by the injection of 1µl of standards at different concentration. Calibration curves plotted from different concentration were obtained for analytes by regression analysis of peak area versus injection concentration. Figure 3.5 and 3.6 show the relation between detector response (area under the curve) and concentration of pesticide. The plot shows the linearity of the detector with malathion

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

8th International Conference
on
Chemical & Environmental
Engineering
19 – 21 April 2016

with R^2 value higher than 0.97 and with dimethoate with R^2 value higher than 0.98 over the studied concentration range, which indicate good linearity.

Figure 3.5 and 3.6 present the determined linearity of the detector with malathion and dimethoate, respectively. The linear range of the detector with malathion covers the concentration range from 0.04038 to 1212 mg/l. the linear range of the detector with malathion has been divided in to three parts, the first part from concentration range 0.04038 to 92 mg/l with correlation coefficient (R^2) = 0.978, the second part from concentration range 92 to 606 mg/l with correlation coefficient (R^2) = 0.996 and the last part from concentration range 606 to 1212 mg/l with correlation coefficient (R^2) = 0.997. The linear range of the detector with dimethoate covers the concentration range from 2.9 to 1754.4 mg/l. The linear range of the detector with dimethoate has been divided in to two parts, the first part from concentration range 3.8 to 135 mg/l with correlation coefficient (R^2) = 0.984 and the second part from concentration range 135 to 1754.4 mg/l with correlation coefficient (R^2) = 0.994

3.4 Accuracy and Precision measurement for the analysis of Malathion and Dimethoate by GC-FPD-S mode

The percentage relative standard deviation (RSD) as precision and percentage relative error (Er %) as accuracy of the suggested methods are calculated. As shown in table 3.5 and 3.6

Table 3.5 Five injection of Malathion (757 mg/l) in GC-FPD-S-mode

Sample no.	Area count	Conc. according to calibration curve (mg/l)
1	20188326	827.9
2	19995406	818.7
3	20046888	821.2
4	20101242	823.8
5	19401786	790.1
Mean		816.4
Er%	7.738%	
Precision	1.569%	

Table 3.6 Five injection of dimethoate (323 mg/l) in GC-FPD-S-mode

Sample no.	Area count	Conc. according to calibration curve
1	12405882	335.0
2	13298656	375.4
3	13184756	370.2
4	13127603	367.6
5	11815867	308.3
Mean		351.3
Er%	8.753%	
Precision	4.988%	

The relative standard deviation (RSD) of the peak areas of the pesticides are 1.569% and 4.988% for malathion and dimethoate, respectively. These values of validation parameters indicated that the analysis using the GC-FPD-S mode method is quite repeatable. The deviation should be in a range similar or better than those obtained in other studies using GC-FPD-S mode (6%) [12].

3.5 Determination of Limit Of Detection (LOD) and Limit Of Quantification (LOQ) for the Detector (FPD-S mode) with Malathion and Dimethoate

LOD and LOQ are established for the methods by the analysis of ultra-pure samples (malathion, dimethoate) with decreasing concentrations until reaching the lowest detectable level. As shown in figures 3.7 and 3.8 these values are 0.0135 and 1.5 mg/l for malathion and dimethoate respectively. On the other hand the lowest determinable level is 0.0404 and 2.9 mg/l for malathion and dimethoate respectively as shown in figure 3.9 and 3.10. The obtained results from the method show good sensitivity for the separation of malathion instead of dimethoate, this may be due to the differences in the chemical and physical properties of the injected organic compounds (malathion and dimethoate) and their interaction with the stationary phase which are the basis of the separation process. The sample components are usually held on the stationary phase so strongly that they are eluted very slowly as the case of dimethoate which has small polarity instead of malathion which is non polar compound [13].

4. Conclusion

The study of air-to-fuel ratio in flame photometric detector in the analysis of Malathion and Dimethoate samples showed the validity of Gas Chromatography-Flame Photometric Detector (S-mode) providing excellent separation and peak shape with high sensitivity. The

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

**8th International Conference
on
Chemical & Environmental
Engineering**
19 – 21 April 2016

method is precise, reproducible, simple, rapid, has a wide range of linearity and dynamic range over a wide range of analyte concentrations with correlation coefficient (R^2) = 0.997 and (R^2) = 0.997 and the relative standard deviation (RSD) 1.569% and 4.988% for malathion and dimethoate respectively and uses small volumes of solvents and samples, reducing the risk for human health and the environment. Besides, the results of this study show that the proposed method could be further applicable to determine the residues of different pesticides in environment.

5. References

[1] Alfonta, L., Katz, E. andWillner, I. (2000), Anal. Chem. 72, 927.
[2] Li, Y.-G., Zhou, Y.-X., Feng, J.-L., Jiang, Z.-H. and Ma, L.-R. (1999), Anal. Chim. Acta 382, 277.
[3] Campanella, L., de Luca, S., Sammartino, M.P. andTomassetti, M. (1999), Anal. Chim. Acta 385, 59.
[4] Marty, J.-L., Mionetto, N., Noguer, T., Ortega, F. and Roux, C. (1993), Biosens. Bioelectron. 8, 273.
[5] Mionetto, N., Marty, J.-L. and Karube, I. (1994), Biosens. Bioelectron. 9, 463.
[6] Lenigh, R., Lam, E., Lai, A., Wang, H., Han, Y., Carlier, P. and Renneberg, R. (2000), Biosens. Bioelectron. 15, 541.
[7] MAREK BANASIK, TODD STEDEFORD, AMANDA S. PERSAD"Selective Inhibition of Acetylcholinesterase in the Cerebellum and Hippocampus of Mice Following an Acute Treatment with Malathion",Journal of Enzyme Inhibition and Medicinal Chemistry, December 2003 Vol. 18 (6), pp. 551–555
[8] WHO, "Malathion in Drinking-water", WHO/SDE/WSH/03.04/103 English only, 2004.
[9] A. Ayman, Gouda Alaa S. Amin Ragaa El Sheikh, "sensitive spectrophotometric method for determination of some organophosphorus pesticide in sample", Chemical Industry & Chemical Engineering Quarterly 16 (1) 11−18 (2010).
[10] WHO. Environmental Health Criteria monograph "Dimethoate", WHO, Geneva, (1989).
[11] ASTM Standard E-840-95 (Reapproved 2000), "Practice for Using Flame Photo metric Detectors in GC", American Society for Testing and Materials, Philadelphia, PA, 1995.
[12] M Hans-Gerd, A Carel, Hai Pham Tuan, Janssen. Cramers, " Evaluation of the Performance of Various Universal and Selective Detectors for Sulfur Determination in Natural Gas ", (1995).
[13] P. W. Scott Raymond, "principle and practice of chromatography", book 1 Chrom-Ed Book Series, (2003).

Military Technical College
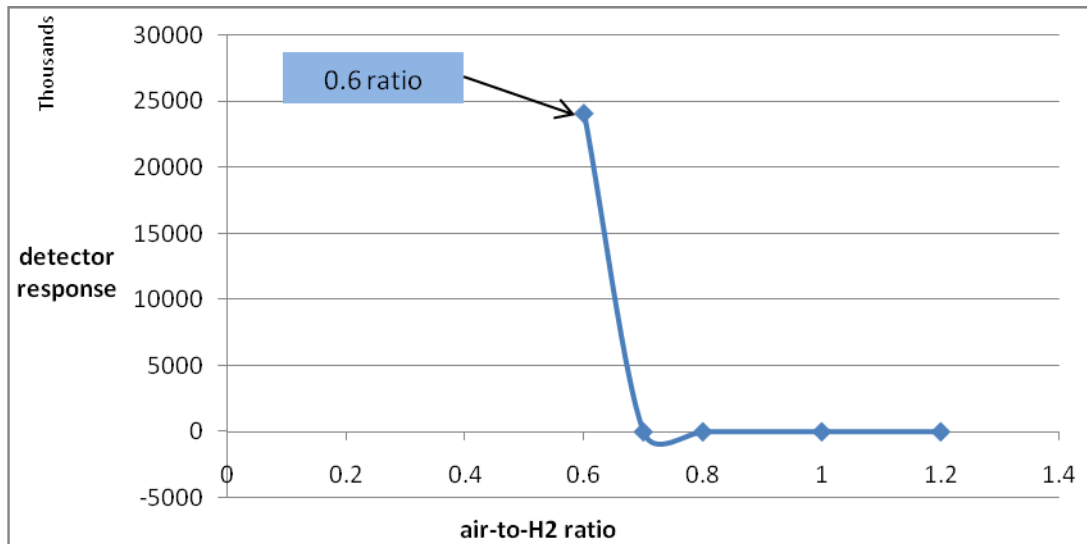Kobry El-Kobbah,
Cairo, Egypt

**Fig.3.1 Detector response with different air-to-H_2 ratio during the analysis of
Malathion by GC-FPD-S mode**
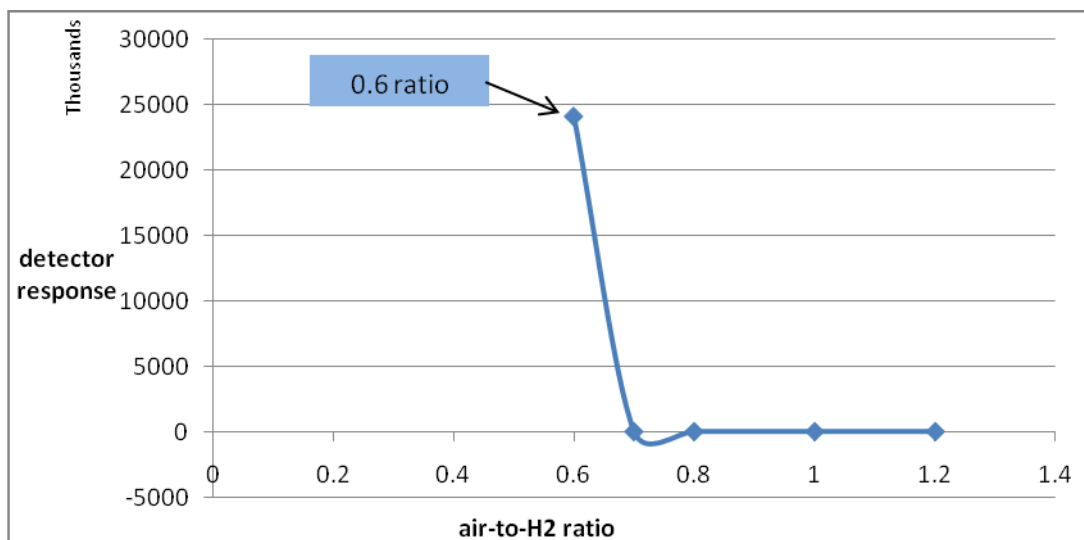
**Fig.3.2 Detector responses with different air-to-H_2 ratio during the analysis of
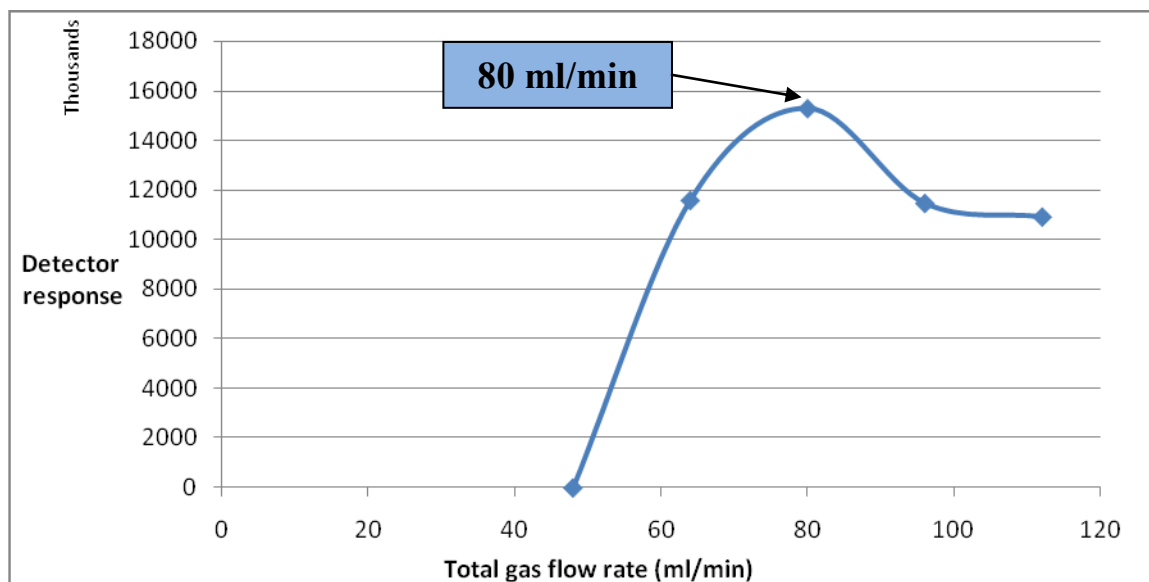dimethoate by GC-FPD-S mode**

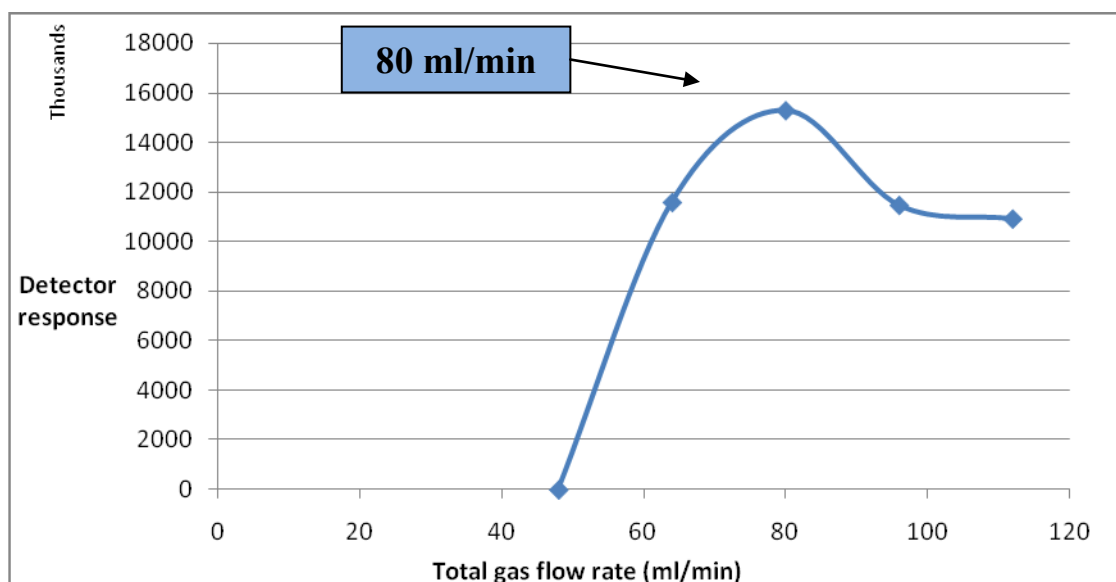**Fig.3.3 Detector response with different total gas flow rates during the analysis of Malathion in by GC-FPD-S-mode**

Fig.3.4 Detector response with different total gas flow rates during the analysis of Dimethoate by GC-FPD-S-mode

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

**8ᵗʰ International Conference
on
Chemical & Environmental
Engineering**
19 – 21 April 2016
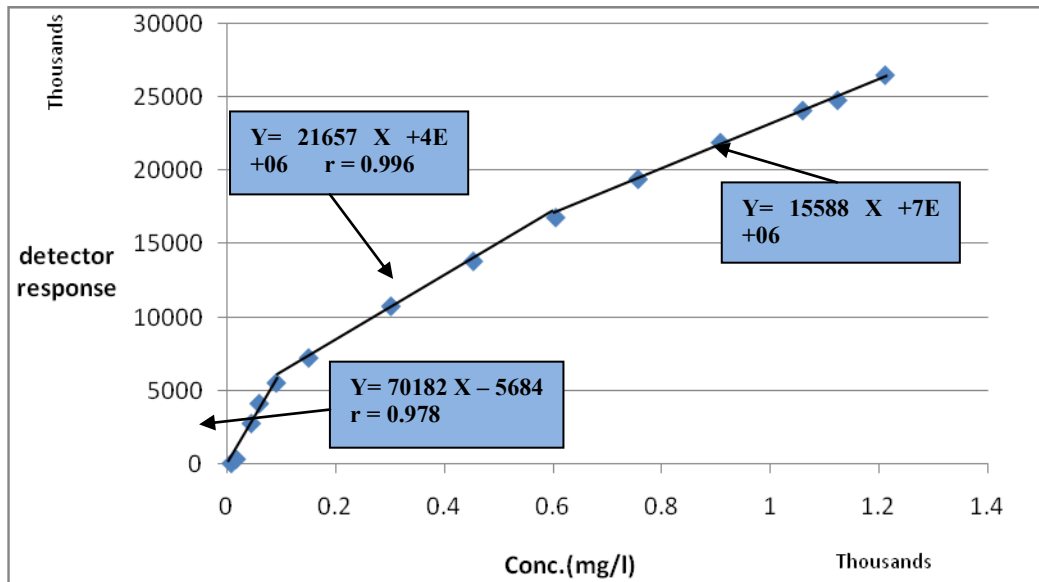
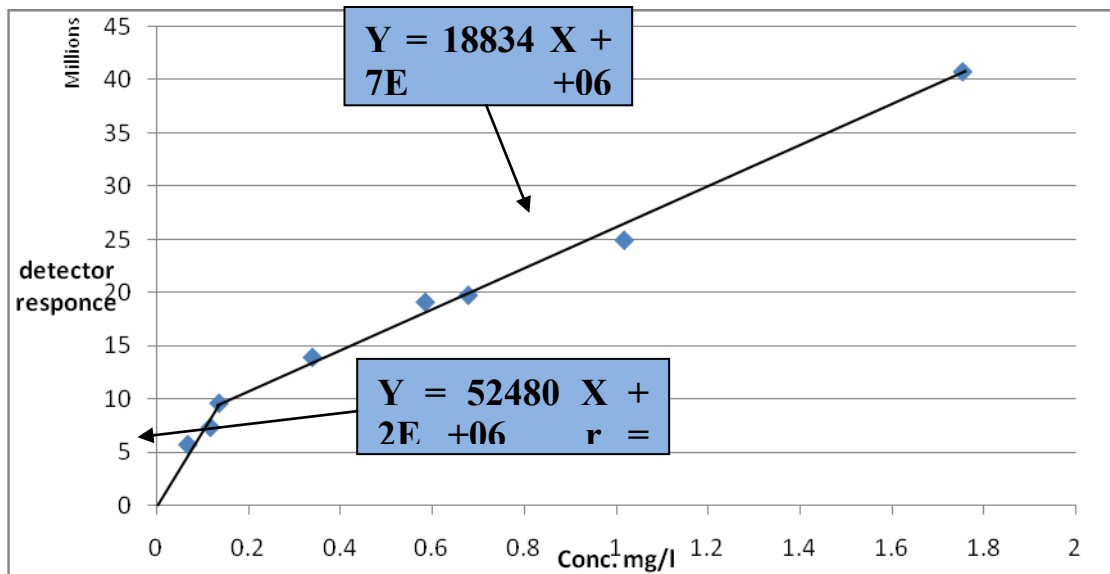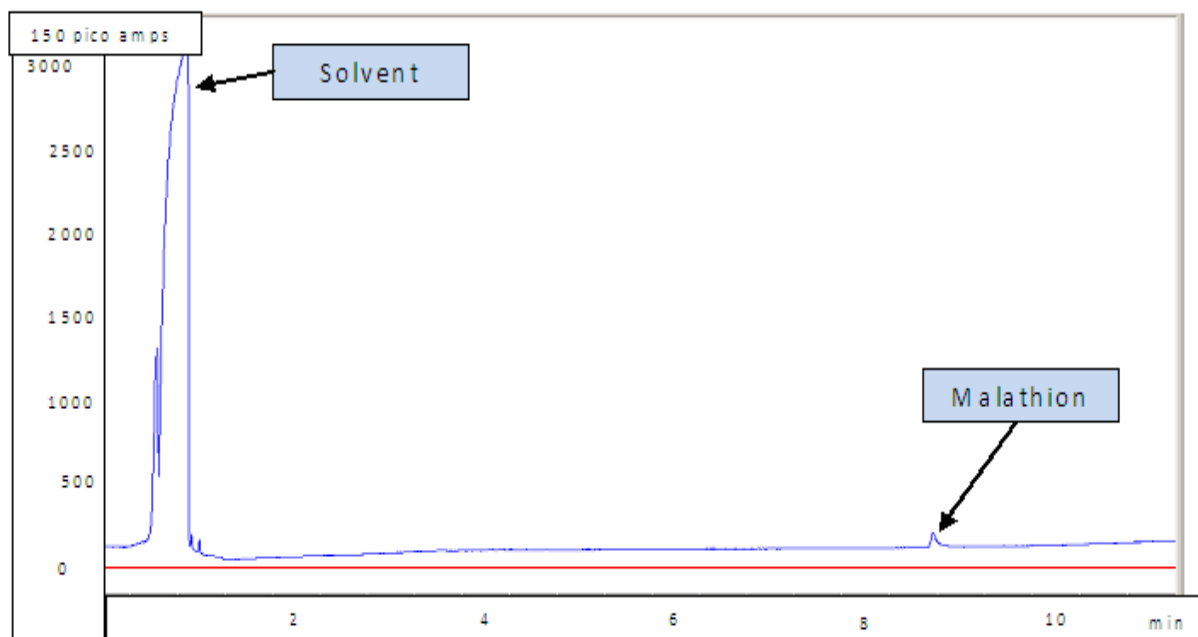**Fig.3.5 Linear range for FPD-S-mode with malathion under specified operating condition**

Fig.3.6 Linear range for FPD-S-mode with dimethoate under specified operating condition

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

**8th International Conference
on
Chemical & Environmental
Engineering**
19 – 21 April 2016

Fig. 3.7 GC-FPD- (S mode) chromatogram of 0.0135 mg/l malathion (LOD), at optimum condition
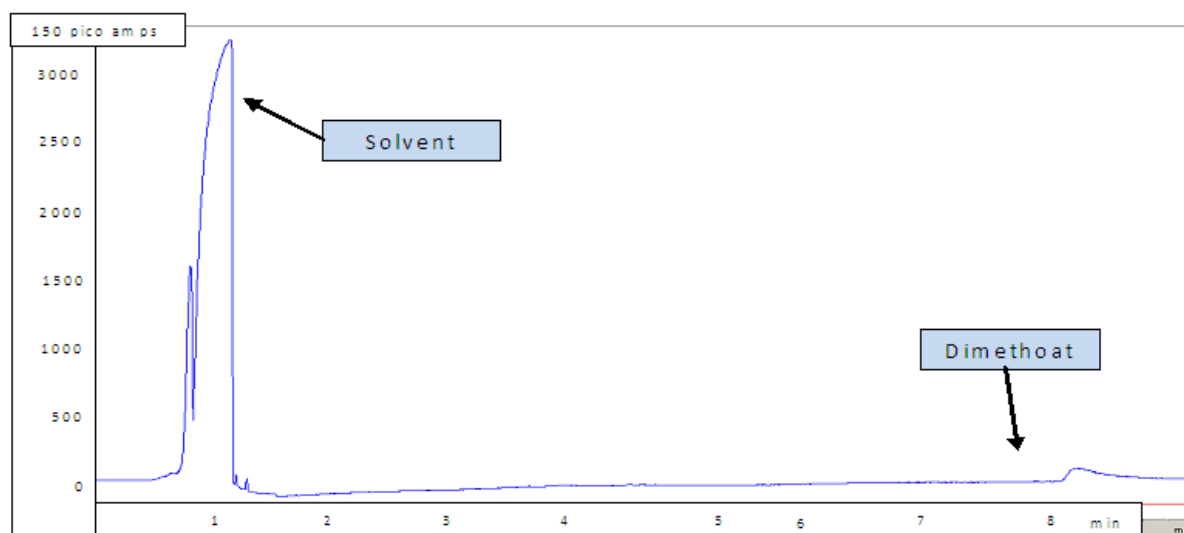

Fig .3.8 GC-FPD- (S mode) Chromatogram of 1.5 mg/l dimethoate (LOD), at optimum condition

153

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

**8ᵗʰ International Conference
on
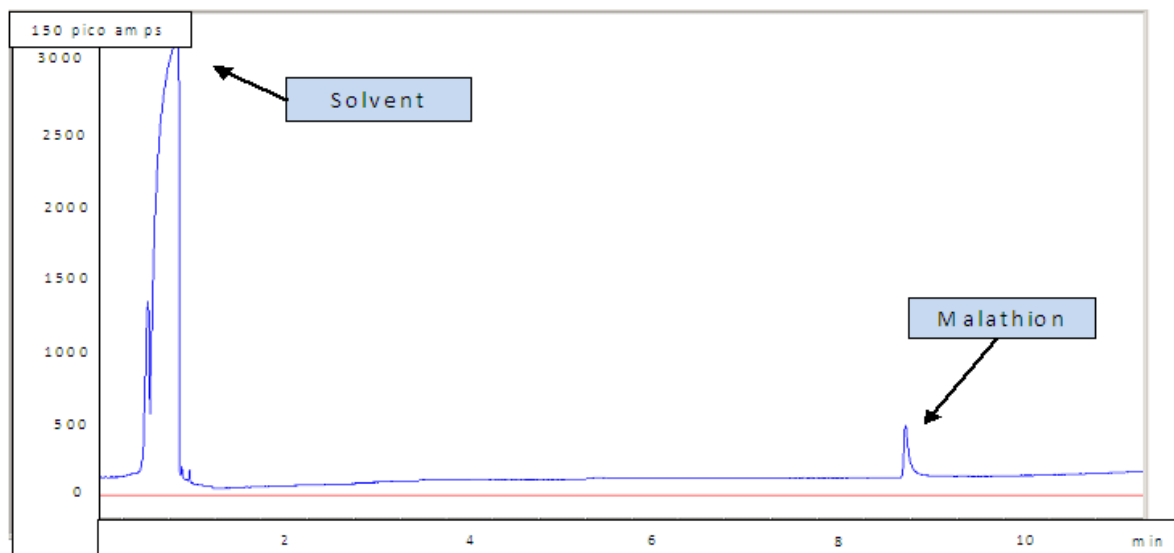Chemical & Environmental
Engineering**
19 – 21 April 2016

Fig. 3.9 GC-FPD- (S mode) Chromatogram of 0.04, 04 mg/l malathion (LOQ), at optimum condition
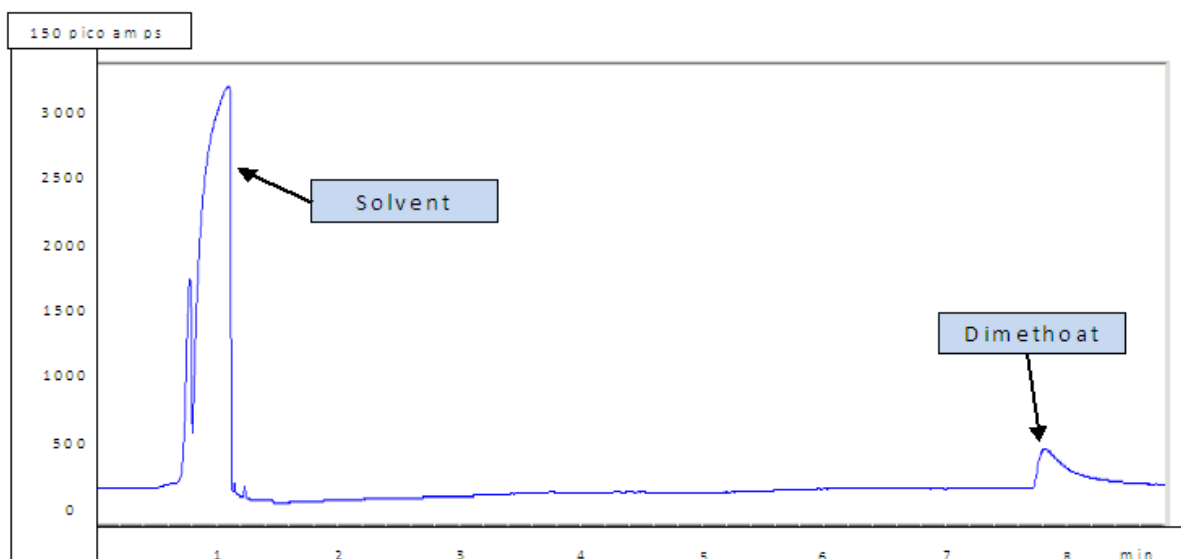

Fig. 3.10 GC-FPD- (S mode)Chromatogram of 2.9 mg/l dimethoate (LOQ), at optimum condition