Determination of vapour pressure of permethrin technical pesticide using gas saturation method with gas chromatographic method

Karri. Apparao[1]*, M.S. Surendra Babu[2], N. Krishna Rao[1], G. Kumar[1] and Tentu. Nageswara Rao[1]
[1]Department of Chemistry, Krishna University, Machilipatnam, A.P, (INDIA)
[2]Department of Chemistry, GITAM University, Hyderabad Campus, Telangana, (INDIA)
E-mail: tnraochemistry@gmail.com

ABSTRACT

The vapour pressure of permethrin technical was conducted using the gas saturation method based on the regulatory OPPTS 830.7950 and EEC A.4 guidelines. According to this method the packed vapour saturator columns were connected to vapour pressure apparatus and the columns were exposed to different flow rates. The flow rates were 20 (F1), 40 (F2) and 60 mL/min (F3). This set up was equilibrated at 40°C for whole night. After equilibration the nitrogen gas outlet from the column was connected to the trapping system. Nitrogen gas was continuously passed through each saturator column. The maintained flow rate and temperatures were monitored during the study period. At the end of 10 days, the trapping agent was collected from the trapping system by eluting the glass columns using 100 mL of acetone. The collected eluate was concentrated using rotary vacuum evaporator to near dryness, and diluted to specific volume using acetone. The samples were analyzed by validated GC method. The vapour pressure of the test item permethrin Technical was found to be 2.08 ×10-6 Pa at 20°C and 6.58 × 10-6 Pa at 40°C.   © 2016 Trade Science Inc. - INDIA

INTRODUCTION

The vapor pressure of solid & liquid compounds can be helpful to decide the thermodynamics stability and time span of usability of an assortment of items, particularly those from the pharmaceutical business[1-3]. The precise capability of vapor pressure can be vital for the sheltered utilize and treatment of strong mixes[4-7]. Vapor pressure (VP) is an imperative component for the investigation of the natural destiny, transport and appropriation of the mixes in water, air and soil[8]. For natural toxins, their VP decides their circulation between the environment and the soil. The vapor pressure of harmful chemicals can be utilized to assess the rate of evaporation after a spill[9-11]. Vapor pressure information is additionally utilized as a part of the estimation of viscosity, enthalpy of vaporization, air-water segment coefficient, and some other critical Physico-Chemical properties of the mixes[12].

Permethrin is in class of compounds called synthetic pyrethroids. Synthetic Pyrethroids are synthesized derivatives of evidently taking place pyrethrins, which are taken from extracts of dried chrysanthemum flowers. Synthetic pyrethriods are greater strong than herbal

pyrethroids, and consequently longer lasting within the area. Although synthetic pyrethroids are frequently thought of as "safe as chrysanthemums", they may be chemically engineered to be more toxic than herbal pyrethroids. Permithrin is widely used as an insecticide in agriculture, houses, gardens and for treatment of ectoparasites (fleas, lice, scabies) on human beings and animals. International, the dominant use of peremthrin is for cotton, which debts forover 60% of the permethrin used[13]. Inside the U.S., nearly 70% of the permethrin utilized in agriculture is used on corn, wheat and alfalfa. Annually, over a hundred million programs of permethrin are made every yr in and around U.S. homes15. Some not unusual merchandise containing permethrin because the lively component consist of: Nix, Elimite, Prelude, combat, Ambush, Dragnet, Outflank, Pounce, Perthrine, picket and Astro. Permethrin comes in amny bureaucracy, inclusive of sprays, dusts, fogs, emulsifiable concentrates and creams. Additionally, in 2003, the EPA permitted permethrin-impregnated apparel for public use[14].

EXPERIMENTAL

Materials and methods

The analytical standard of peremthrin (95.3%) and the sample of peremthrin (95.2%) were obtained from Sigma Aldrich. The HPLC grade solvent acetone from Rankem, New Delhi. Reagent water used in this study was demineralized and purified using a Millipore Milli-Q Purification Water System. Sea sand sourced from Machilipatnam, India, sea sand was used as solid support for the test item within the saturator columns. The sea sand was sieved to get uniform size particles. The sand was washed prior to use with sulphuric acid, Milli-Q® water followed by acetone and dried at approximately 120°C. Nitrogen gas (Purity 99.999%) supplied by BOC India Ltd., Mumbai, India, was used as carrier gas in this study.

Silica gel of mesh size 60 to 120 supplied by Merck limited, Mumbai, India was used as a trapping agent to collect Permethrin technical vapour. A digital temperature controlled vapour pressure apparatus, supplied by Labindia Instruments Private Limited, Chennai, India, was used in this study. The carrier gas flow rate was measured using manual flow meter supplied by Shimadzu

Corporation, Japan. Stainless steel columns of 60 cm × 15 mm dimensions fitted with adapters at both ends were used in this study. The trapping material (10–11 g of silica gel) was packed in flexible polypropylene tubes having both ends plugged with cotton swabs. The outlet of the stainless steel saturator column was connected to the polypropylene tubes filled with silica gel. To measure the gas flow, a manual flow meter was connected at the trap end. Buchi rotavapour temperature controlled vacuum rotary evaporator - M/s. Buchi Labortecnik, AG, Switzerland was used in this study. A hot air oven supplied by Scientific Systems, Chennai, India was used in this study.

Chromatographic separation parameters

The GC system used, consisted shimadzu Gas chromatography with Electron Capture Detector, interfaced with GC solution software, equipped with a mega bore GC column of 30m length x 0.53mm I.D. x 1.0μm (DB-1) with 80 kPa Nitrogen (N_2) Gas flow rate, Column oven temperature was maintained at 300°C, injector temperature was maintained at 300°C, Detector temperature was maintained at 300°C and the injected sample volume was 1.0 μL. The retention time of permethrin approximately 2.5 minutes.

Linearity of response

A stock solution of permethrin technical was prepared by weighing 4.94 mg of 93.5% purity reference standard into a 10mL volumetric flask and bringing to volume with acetone. A series of calibration solutions were then prepared by diluting the appropriate volume of stock solution into different 10 mL volumetric flasks and bringing to volume with acetone. The prepared calibration solutions 0.01 mg/L, 0.05 mg/L, 0.1 mg/L, 0.5 mg/L, 1.0 mg/L and 10 mg/L were injected into a Gas Chromatography. A linear curve was plotted for the concentration of standard versus observed peak area, and the correlation coefficient was determined.

Method specificity

Silica gel control was assayed to check the method specificity.

Recovery from trapping agent

The recovery test was performed in order to

Full Paper

validate the analytical method for Permethrin analysis. Approximately 10 g of silica gel was weighed and this was fortified with the Permethrin analytical standard at the concentration levels 0.03 µg/g (S1), 0.3 µg/g (S2). Each concentration was fortified for 5 times and were coded as S1(S1R1, …S1R5), S2(S2R1, …S2R5). The replicates were transferred to glass chromatographic columns and extracted with 100 mL acetone. The extract from each column was concentrated to near dryness and reconstituted with 10 mL acetone before quantification. Two control samples were maintained (S0R1 and S0R2) using unfortified sand.

Preliminary test

Preparation of the saturator columns

Accurately 3.10 g of permethrin technical was weighed and added to a 180 g of sea sand. The treated sand was thoroughly mixed. The saturator columns were prepared by weighing and packing 60 g of treated sand into three stainless steel columns (length 60 cm and diameter 15 mm). The columns were coded C1 through C3. The remaining test item coated sand was packed in HDPE container and refrigerated for stability analysis after preliminary test.

Flow rate selection

The packed vapour saturator columns were connected to vapour pressure apparatus and the columns were exposed to different flow rates. The flow rates were 20 (F1), 40(F2) and 60 mL/min (F3). This set up was equilibrated at 40°C for whole night. After equilibration the nitrogen gas outlet from the column was connected to the trapping system. Nitrogen gas was continuously passed through each saturator column. The maintained flow rate and temperatures were monitored during the study period. At the end of 10 days, the trapping agent was collected from the trapping system by eluting the glass columns using 100 mL of acetone. The collected eluate was concentrated using rotary vacuum evaporator to near dryness, and diluted to specific volume using acetone. The samples were analysed by Gas Chromatography.

Stability confirmation

The coated sand from day 0 and from column C2 after 10 days of incubation was weighed in triplicate and eluted with 100 mL acetone in glass columns. The

eluate was evaporated to near dryness and diluted using acetone before quantification by Gas Chromatography.

Definitive test

Accurately 6.13 g of permethrin technical was weighed and added to 360 g sea sand. The treated sand was thoroughly mixed. The stainless steel saturated column were then filled with permethrin technical coated sea sand. The columns were then placed in the vapour pressure apparatus. The column inlets were connected to nitrogen flow and this set up was equilibrated at 20°C and 40°C overnight. After equilibration the nitrogen gas outlets from the columns were connected to the trapping system.

The nitrogen gas was allowed to flow through the column and traps at a fixed rate of 40 mL/min. The experiment was continued for 10 days. The column chamber temperature and flow rate was measured thrice per day. The remaining treated sand was stored in a HDPE container and refrigerated for stability analysis after the definitive test.

After 10 days, the trapping agent (silica gel) was collected from the trapping system. The trapping agent was transferred to glass columns and the test item was eluted using 100 mL of acetone. The eluate was concentrated using a rotary vacuum evaporator, diluted using acetone to a specific volume (1 mL for Te1 and Te2) and analysed for Permethrin technical content. The test item coated sand pertaining to 0 day and pertaining to column Te1R2 was checked for stability.

RESULTS AND DISCUSSION

Method validation

Linearity of response

A plot of the found peak area of permethrin and

TABLE 1 : Linearity for permethrin technical

Permethrin concentration (µg/ml)	Peak Area (µV-Sec)
0.01	517
0.05	2576
0.1	5167
0.5	20073
1	55840
10	505612
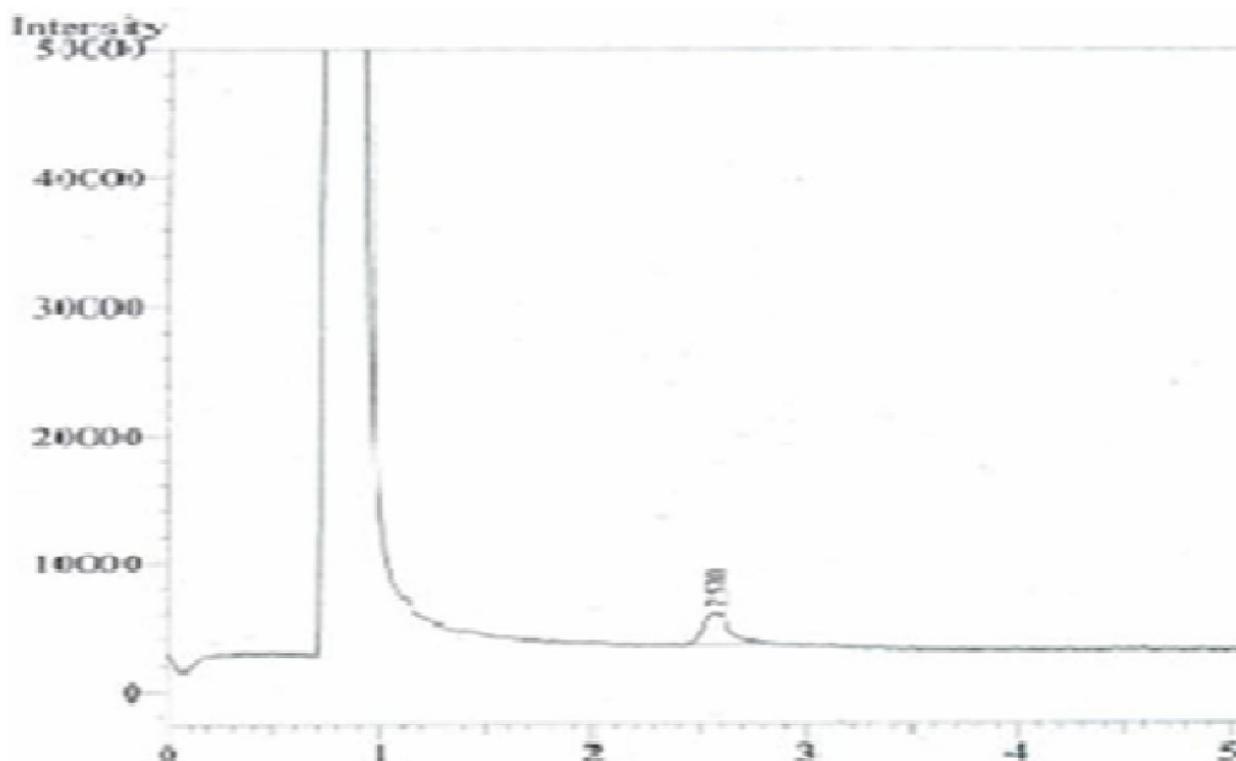
Figure 1 : Representative chromatogram of permethrin calibration solution (0.5 mg/L)

TABLE 2 : Recovery of permethrin technical from trapping agent (silica gel)

Code	Fortified Concentration of Permethrin technical(μg/g)	Total Recovered Permethrin technical(μg/g)	Recovery (%)	Average Recovery (%)	Relative Standard Deviation (%)
S0R1	NF	NF	-	NF	NF
S0R2	NF	NF	-		
S1R1	0.03	0.0284	94.7		
S1R2	0.03	0.0297	99.1		
S1R3	0.03	0.0294	98.1	97.21	2.512
S1R4	0.03	0.0299	99.7		
S1R5	0.03	0.0284	94.5		
S2R1	0.3	0.2891	96.4		
S2R2	0.3	0.2989	99.6		
S2R3	0.3	0.2882	96.1	97.90	1.767
S2R4	0.3	0.2933	97.8		
S2R5	0.3	0.2990	99.7		

NF – Not Fortified

Full Paper
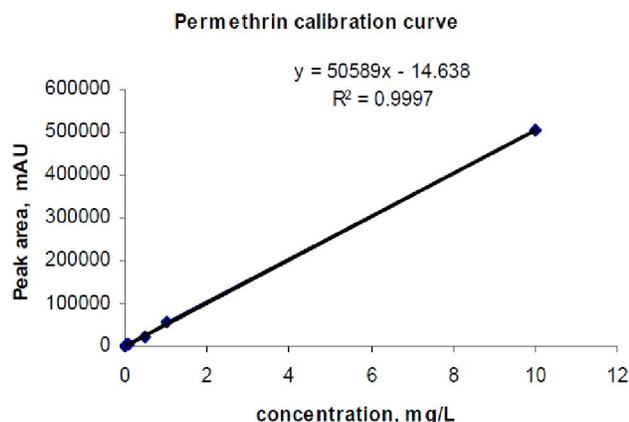
Figure 2 : Typical permethrin technical calibration curve

the concentration in the standard solutions showed acceptable linearity, as indicated by the correlation coefficient of 0.9999. The data are presented in TABLE 1. A representative calibration curve is presented in Figure 2 and chromatogram are presented in Figure 1.

Method specificity

No significant interference was observed from silica gel control.

Recovery from trapping agent (Silica Gel)

Recovery studies conducted with the trapping agent at two concentrations 0.03 μg/g and 0.3 μg/g showed an acceptable recovery of 97.21 and 97.90%, respectively. The percentage relative standard deviation (RSD) was 2.442 and 1.730 for the 0.03 μg/g and 0.3 μg/g samples, respectively. The results are presented in Error! Reference source not found.. A representative chromatogram is presented in Figure 3.

Preliminary test

The preliminary test was conducted at 40°C with three different carrier gas flow rates. The results are summarized in the following table:

Sample Code	Temperature (°C)	Carrier Gas * Flow-Rate (mL/min)	Volume Carrier Gas (m³)	Amount Trapped (mg)	Concentration (mg/m³)
F1		20	0.2880	0.0001	0.000412
F2	40	40	0.5760	0.0005	0.000943
F3		60	0.8640	0.0006	0.000712

*Average flow rate calculated for 10 days
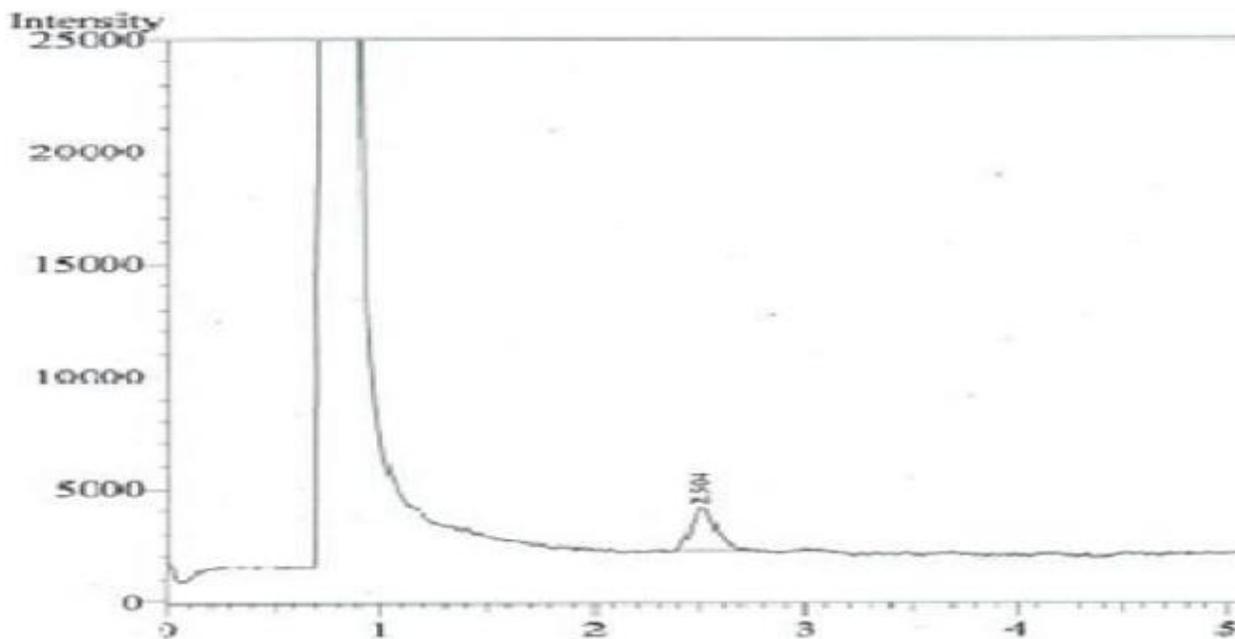
Figure 3 : Representative chromatogram of permethrin technical from the trapping system recovery experiment

Karri. Apparao et al.

TABLE 3 : Stability of permethrin technical from the coated sand samples – preliminary study – 10th day

Temperature °C	Sample ID	*Dosing Level (g/kg)	Recovered (g/kg)	Recovery %
	T2R1	18.25	18.53	101.54
40	T2R2	18.25	17.75	97.27
	T2R3	18.25	17.82	97.66
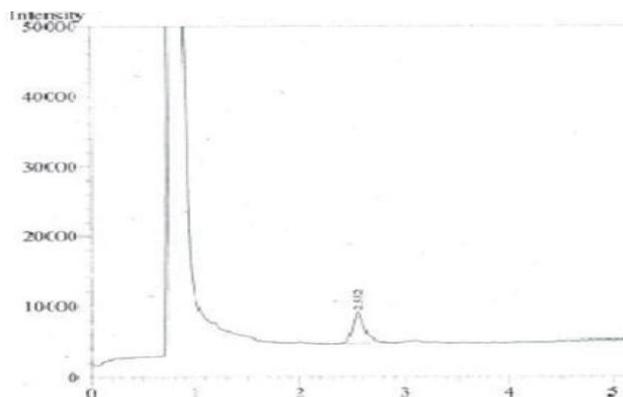
Figure 4 : Representative chromatogram of permethrin technical from coated sand at 40°C

Based on the results above, a nitrogen flow rate of approximately 40 mL/min was selected for definitive test. The carrier gas was in saturation equilibrium with Permethrin technical at this flow rate.

Stability confirmation

The results presented in Error! Reference source not found. clearly shows that permethrin technical was stable during the 10 day storage period at 40°C. The average recovery of triplicate analysis of 1 g samples after 10 days of storage was 98.82% at 40°C. Representative chromatogram is presented in Figure 4.

Definitive test

In the definitive experiment, three replicate sea sand samples coated with Permethrin technical were tested at two different temperatures (20 and 40°C) for a period of 10 days, using a carrier gas flow rate of approximately 40 mL/min. TABLE 4 presents the temperature and flow rate data. Analysis of the sorbent

TABLE 4 : Temperature and flow rate data during vapour pressure determination of permethrin technical - definitive test

Days	Temperature (°C)		Average Flow Rate (mL/min)*					
	Oven 1	Oven 2	Oven 1			Oven 2		
			Te1R1	Te1R2	Te1R3	Te2R1	Te2R2	Te2R3
0	40	20	40	40	40	40	40	40
1	40	20	40	40	40	40	40	40
2	40	20	40	40	40	40	40	40
3	40	20	40	40	40	40	40	40
4	40	20	40	40	40	40	40	40
5	40	20	40	40	40	40	40	40
6	40	20	40	40	40	40	40	40
7	40	20	40	40	40	40	40	40
8	40	20	40	40	40	40	40	40
9	40	20	40	40	40	40	40	40

* Average flow rate of three measurements

TABLE 5 : Determination of vapour pressure of permethrin technical at 40°C

Sample ID	W (g)	V (m3)	P (Pa) at 40°C
Te1R1	5.72 X 10-7	0.5760	6.60 x 10-6
Te1R2	5.80 X 10-7	0.5760	6.70 x 10-6
Te1R3	5.57 X 10-7	0.5760	6.43 x 10-6
Average	5.69 x 10-7	0.5760	6.58 x 10-6
Standard Deviation			1.35 x 10-7

TABLE 6 : Determination of vapour pressure of permethrin technical at 20°C

Sample ID	W(g)	V(m3)	P (Pa) at 40°C
Te2R1	1.94 x 10-7	0.5760	2.10 x 10-6
Te2R2	1.89 x 10-7	0.5760	2.04 x 10-6
Te2R3	1.94 x 10-7	0.5760	2.09 x 10-6
Average	1.92 x 10-7	0.5760	2.08 x 10-6
Standard Deviation			2.90 x 10-8

Full Paper

traps maintained at 20°C experiment showed the average mass of permethrin technical collected after 10 days as 1.92×10^{7} g. Analysis of the sorbent traps maintained at 40°C experiment showed the mass of

TABLE 7 : Stability of permethrin technical from the coated sand sample – definitive study

Temperature °C	Sample ID	*Dosing Level (g/kg)	Recovered (g/kg)	Recovery %
	T4R1	17.97	17.90	99.61
20	T4R2	17.97	17.34	96.49
	T4R3	17.97	17.83	99.20

*Average of Three Replicates - 0th days after Storage : 100% (17.97 g/kg); 10th Day after : 98.43%; Nitrogen Purge at 20°C

permethrin technical collected after 10 days as 5.69×10^{-7} g. Representative chromatograms from the analysis of the sorbent traps at 20°C and 40°C experiments are presented in Figure 5 and Figure 6.

Using the mass of the permethrin technical collected during the experiment and the total volume of gas used, the vapour pressure of the permethrin technical at 40°C and 20°C was calculated. The results are presented in Table and Error! Reference source not found.. From the data, the average vapour pressure value of permethrin technical at 20°C was 2.08×10^{-6} Pa and at 40°C was 6.58×10^{-6} Pa. The results presented in Table clearly show that test item permethrin technical is stable during the 10 days storage period at temperature
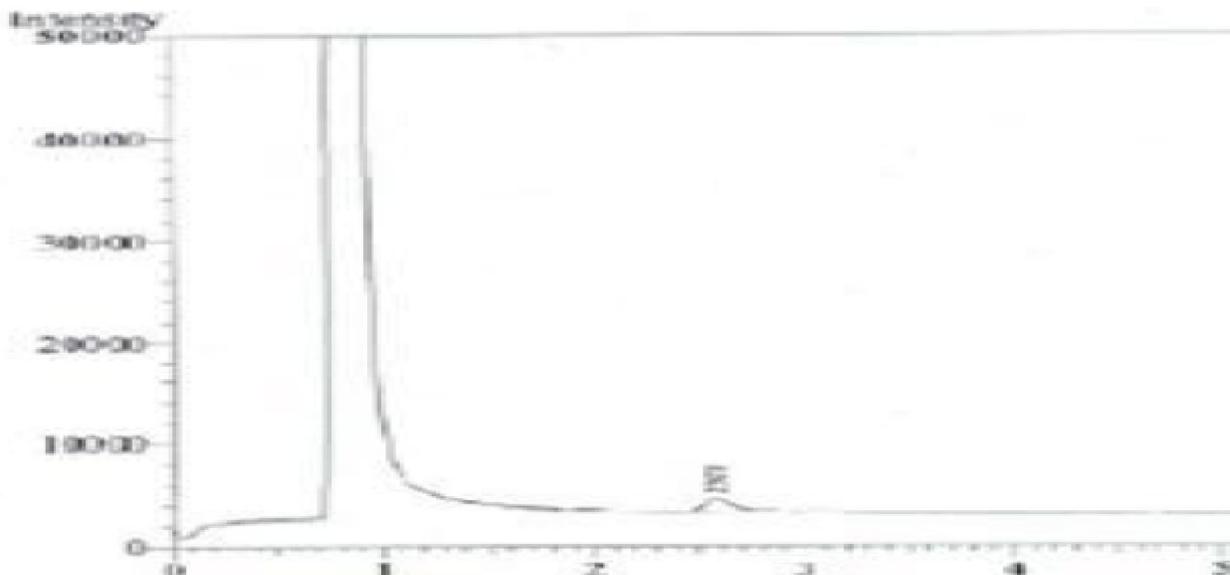
Figure 5 : Representative chromatogram of permethrin technical from the 20°C definitive study
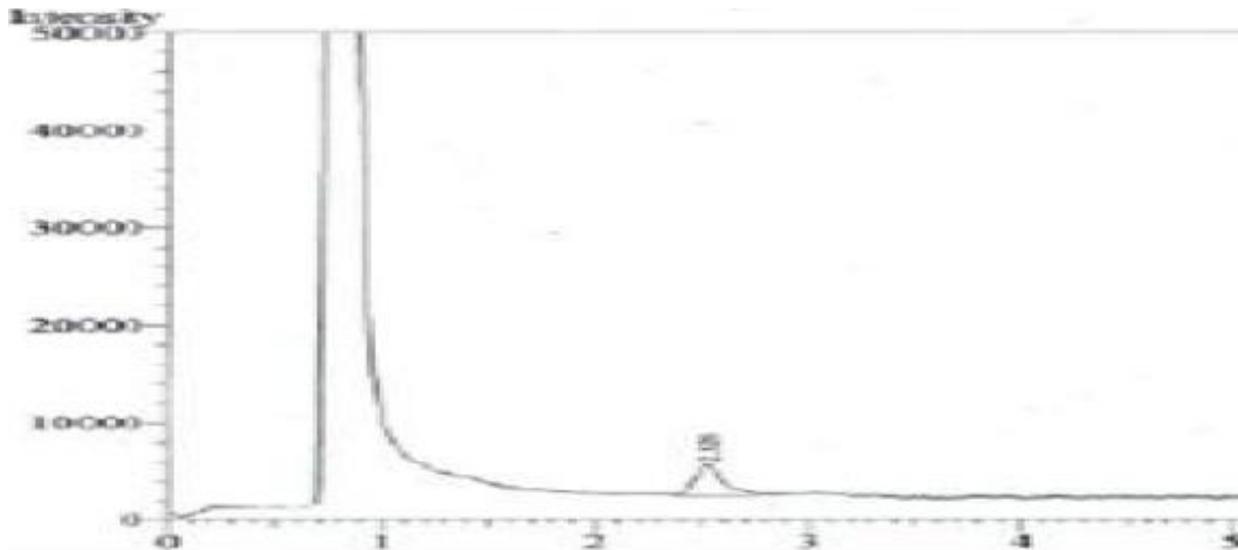
Figure 6 : Representative chromatogram of permethrin technical from the 40°C definitive study

Full Paper

20°C. The average recovery of triplicate analysis of 1 g of samples after 10 days of storage was 98.43%.

CONCLUSION

The vapour pressure of permethrin technical at 20°C was 2.08 × 10-6 Pa and at 40°C was 6.58 × 10-6 Pa.

ACKNOWLEDGEMENT

The authors are thankful to the Dr. B. Gowtham Prasad, SVV University, for providing necessary facility to conduct the Laboratory experiment.

REFERENCES

[1]   W.F.Spencer, M.M.Cliath; Residue Reviews., **85**, 57-71 **(1983)**.

[2]   A.L.Goel, LL.Connell, A.Torrents; J Envoron Sci Health B., **42**, 343-3499 **(2007)**.

[3]   B.Terece Grayson, Eric Langner, David Wells; Pesticide Science., **13**, 552-556 **(1982)**.

[4]   Mc Clelland, P.C.Jurs; Journal of Chemical Information and Computer Science., **40**, 967- 975 **(2000)**.

[5]   K.C.P Prem; Organic & Biomolecular Chemistry., **3**, 1176-1179 **(2005)**.

[6]   A.Daniel, Hinckley, F.Terry Bidleman, T.William, Foreman, R.Jack, Tuschall; J.Chem.Eng. Data., **35**, 232-237 **(1990)**.

[7]   Jaakko Paasivirta, Seija Sinkkonen, Pirjo Mikkelson, Tiina Rantio, Frank Wania; Chemosphere., **39**, 811-832 **(1999)**.

[8]   Alessandro Delle Site; J.Phys.Chem.Ref. Data. 26, 157 **(1997)**.

[9]   Nicholas J.Fendinger, E.Dwight; Environmental Toxicology and chemistry., **9**, 731-735 **(1990)**.

[10] S.F.Wright, D.Dollimore, J.G.Dunn, K.Alexander; Thermochimica Acta., **421**, 25-30 **(2004)**.

[11] Banu Cetin, Serdar Ozer, Aysun Sofuoglu, Mustafa Odabasi; Atmospheric Environment., **40**, 4538-4546 **(2006)**.

[12] Bouwman, B.Sereda, H.M.Meinhardt; Environmentalpollution., **144**, 902-917 **(2006)**.

[13] N.S.Mirzabekova, N.E.Kuzmina, O.I.Lukashov, N.A.Sokolova, S.N.Golosov, P.V.Kazakov et al; Russian Journal of Organic Chemistry., **45**, 355-359 **(2009)**.

[14] Holmstead, Roy, Casida, E.John Ruzo, O.Luis, Fullmer, G.Donald; J. Agric. Food Chem., **26**, 590-595 **(1978)**.