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Vapor Pressure of Triadimefon by the Gas Saturation Method

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Vapor pressures of triadimefon {1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butanone} were measured between 25 °C and 70 °C, using a gas saturation technique with XAD-2 adsorbent vapor traps. Vapor pressures ranged from $(2.25 \pm 0.24) \times 10^{-4}$ Pa to $(8.72 \pm 0.29) \times 10^{-2}$ Pa. The experimental results were related to temperature by the equation $\log p/\mathrm{Pa} = (15.87 \pm 0.35) - (5802 \pm 113)\mathrm{K}/T$. The calculated molar enthalpy of sublimation was found to be (111.1 ± 2.2) $\mathrm{kJ \cdot mol^{-1}}$ and shows no significant temperature dependence in the temperature range investigated.

Introduction

Vapor pressures of pure substances are among the most important and fundamental physical properties. Reliable vapor pressure data are indispensable to predicting the behavior and fate of chemicals that are introduced into the environment. Volatilization and vapor phase transport from soil, plant, and water systems are largely controlled by the compound's vapor pressure (Spencer and Cliath, 1983). Unfortunately, there is still a lack of data, especially for high molecular weight organics.

Triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butanone, is a systemic fungicide widely used in Portugal, particularly against powdery mildews in commercial greenhouses. Depending on the degree of protection, agrochemicals used indoors may cause problems due to exposure of applicators and workers. Vapor pressures of pure triadimefon are the starting point in evaluating the vapor concentrations inside commercial greenhouses, an important parameter to assess the pesticide exposure to greenhouse applicators and workers.

The gas saturation method is generally accepted as being sufficiently accurate to measure vapor pressures below 1 Pa. This method involves production of a saturated vapor phase by passing an inert gas through a chamber packed with an analyte-coated inert support. The chemical is removed from the carrier gas by a trapping agent and quantified by some suitable method. Spencer and Cliath (1969, 1970, 1972) used sand as an inert support, hexane as a trapping agent, and gas chromatography for the quantification of several pesticides. Since then the method has been modified to use different analytical techniques (Macknick and Prausnitz, 1979; Rothman, 1980; Sonnefeld *et al.*, 1983) and solid adsorption traps such as Florisil (Westcott *et al.*, 1981), XAD-2 (Kuo *et al.*, 1992), Tenax (Skene and Krzymien, 1995; Wania *et al.*, 1994), and polyurethane (Turner and Glotfelty, 1977; Spencer *et al.*, 1979). Recent developments have focused on reducing the amount of material needed (Westcott *et al.*, 1981) and reducing the analysis time (Sonnefeld *et al.*, 1983; Wania *et al.*, 1994).

The vapor pressure of a reference compound should be measured in order to verify the accuracy of any new method. Naphthalene has been recommended by IUPAC as a reference material for the determination of vapor pressures of low-volatility compounds (Ambrose, 1987).

This paper reports the use of a gas saturation technique, with XAD-2 adsorbent vapor traps, to determine vapor pressures of triadimefon between 25 °C and 70 °C. The accuracy of the experimental setup and quantification method were confirmed by reproducing the literature value of naphthalene vapor pressure at 37 °C.

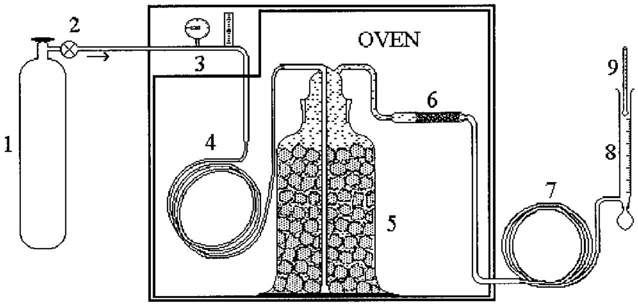

Figure 1. Schematic diagram of the experimental apparatus used to produce and collect the saturated vapor of triadimefon: (1) gas supply; (2) regulator valve; (3) flow controller; (4) warming tube; (5) saturator chamber; (6) XAD-2 trap; (7) cooling tube; (8) soap bubbler; (9) thermometer.

Experimental Section

Materials: triadimefon (offered by Bayer Portugal in its highest grade), Bayleton 5 (wettable powder with 5% (w/w) triadimefon), ethanol (Merck, p.a.), acetonitrile (Merck, LiChrosolv), methanol (Merck, LiChrosolv), deionized and distilled water, dichloromethane (Merck, p.a.), benzene (Merck, p.a.), naphthalene (Panreac, purissimum), ORBO-42SM vapor trap tubes (Supelco Inc.).

Apparatus. A modified version of the vapor generator described by Morabito *et al.* (1990) was used to produce and collect the saturated vapors. The apparatus consisted of several components, as shown in Figure 1: a temperature-controlled saturator chamber, a nitrogen supply, a flow controller, an adsorbent trap, and a gas monitoring device.

The saturator chamber temperature was controlled (±0.1 deg) using the oven of a Shimadzu GC-9A gas chromatograph. The nitrogen carrier flux, controlled by the chromatograph flux controller, was supplied to the saturator chamber through a coiled copper tube, located in the oven, to equilibrate the gas temperature before entering the saturation chamber. The gas stream exiting the saturation chamber was conveyed to an ORBO-42SM vapor trap tube, placed inside the oven. These solvent desorption tubes contain a glass wool filter, a 66 mg sampling bed and a 33 mg backup bed of XAD-2 adsorbent (Supelpak 20), and polyurethane foam plugs. After exiting the trap tube, the flow was conducted outside the oven, thermally equili-

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brated to ambient temperature by a coiled copper tube, and monitored by a soap bubbler flow meter.

The saturator chamber was a 250 mL gas wash bottle filled with sand, which had been coated in a rotary evaporator (Heidolph WB 2000, at 50 °C) by mixing a solution of approximately 5 g of the analyte in dichloromethane with about 500 g of sand. The sand was previously washed in dilute HCl and rinsed in distilled water (Spencer and Cliath, 1983), and the triadimefon used to coat the sand was extracted from the commercial formulation Bayleton 5 with dichloromethane and purified by several recrystallizations in ethanol. High-purity triadimefon is not essential for the coating because it is recognized that impurities do not interfere with this method of measuring vapor pressures (Spencer and Cliath, 1983). For naphthalene the saturator chamber was a 100 mL gas wash bottle filled with the pure compound.

The triadimefon and naphthalene recoveries were studied by replacing the saturator chamber by a small glass recipient containing a known amount of compound. The recoveries were obtained by comparing the amount of triadimefon removed by the gas stream with the quantity retained in the trap.

Analytical Technique. The triadimefon trapped was extracted by passing 5 mL of ethanol through the trap tube. The analyses were performed in an Merck-Hitachi high-performance liquid chromatograph (HPLC), model 655A-11, equipped with a 655A-22 UV detector and the D-2000 integrator. The analysis conditions, already established by us (Da Silva and Da Silva, 1993), were the following: detection at 220 nm, mobile phase 55% acetonitrile and 45% water (v/v), column RP-18 125 mm long × 4 mm i.d., dp 5 μm, flow 1.5 mL/min.

The naphthalene trapped was extracted by passing 5 mL of benzene through the trap tube. The analyses were performed in the same HPLC system with a JASCO 820-FP fluorescence detector. The analysis conditions were the following: excitation at 280 nm, emission at 330 nm, mobile phase 85% acetonitrile and 15% water (v/v), column RP-18 125 mm long × 4 mm i.d., dp 5 μm, flow 1.5 mL/min.

Procedure. The system was allowed to equilibrate with a flowing gas stream for several days before the first measurement. Another equilibration period of 1 day was employed after each temperature change. Saturation vapor pressures p_s were calculated from the ideal gas law

$$p_s = nRT_s/V_g \tag{1}$$

where n is the number of moles of chemical trapped, T_s is absolute temperature of the saturator chamber, V_g is the volume of collected gas at the temperature of the saturator chamber, and R is the gas constant (8.314 $\text{J·mol}^{-1}\text{·K}^{-1}$). In each measurement, the total nitrogen volume passing through the system was obtained from the average flow rate. This volume was corrected for the temperature change between the saturator chamber and the soap bubbler flow meter to obtain V_g. The correction due to the pressure drop across the vapor trap was not done because it was assumed to be negligible since solid traps were used (Spencer and Cliath, 1983). All vapor pressure and recovery studies were made using flow rates between 3.0 and 8.0 mL/min.

The fundamental equation relating the vapor pressure of a solid (p_s) to temperature is the Clapeyron equation

$$\frac{\mathrm{d}p_s}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sub}}H}{T\Delta V} \tag{2}$$

where T is the absolute temperature, $\Delta_{\mathrm{sub}}H$ is the enthalpy of sublimation, and ΔV is the volume change upon sublimation. Assuming the gas is perfect, the volume of the solid is negligible compared to the volume of the gas, and $\Delta_{\mathrm{sub}}H$ is independent of temperature, the integration of eq 2 leads to

$$\log(p_s/\mathrm{Pa}) = A - \frac{B}{(T/\mathrm{K})} \tag{3}$$

where A and B are parameters, B being $\Delta_{\mathrm{sub}}H(2.303\mathrm{R})^{-1}$. The vapor pressure results were correlated to temperature using eq 3, and $\Delta_{\mathrm{sub}}H$ was calculated from the parameter B.

Table 1. Recoveries of Triadimefon at Different Temperatures

t/°C	recovery (%)	t/°C	recovery (%)
30	92	60	83
40	87	70	89
50	90		

Results and Discussion

Vapor Pressure of Naphthalene. Four recovery studies of naphthalene gave a collection efficiency of 88 ± 3% at 37 °C. At this temperature the vapor pressure was found to be (28.8 ± 2.5) Pa (uncorrected for the recovery). The reference value is 34.1 Pa (Ambrose, 1987), suggesting that vapor pressure must be corrected for recovery, yielding (32.9 ± 3.1) Pa. The masses of collected naphthalene (between 0.006 and 0.012 mg) in the vapor pressure determinations and the recovery studies were similar.

Vapor Pressure of Triadimefon. The vapor pressure of triadimefon was determined between 25 °C and 70 °C, at intervals of 5 deg. The technique could also be used to measure vapor pressures at temperatures lower than 25 °C, provided the chromatograph was equipped with a cooling system.

Since the method uses the vapor trap inside the oven, a study was done to know if the recoveries are influenced by the temperature. The results in Table 1 show no significant trends in the range of temperatures studied; hence all vapor pressure values were corrected considering the average recovery of 88%. Using the same tube traps, Thomas and Nishioka (1985) found similar values for the recoveries of DDVP, pyrethrum, and pentachlorophenol.

XAD-2 resin vapor traps have been used to collect quantitatively vapors of 4,4′-bipyridine (Kuo *et al.*, 1992) and pyrethrum (OSHA, 1988a; Thomas and Nishioka, 1985) and organochlorine (OSHA, 1987b; Thomas and Nishioka, 1985), organophosphorus (OSHA, 1986), and carbamate (OSHA, 1988b, 1987a; Thomas and Nishioka, 1985) pesticides. XAD-2 adsorbent is a versatile and easy to handle sampling medium. The method used and the recovery results for naphthalene and triadimefon verify these properties and show that the collection efficiency is not affected by temperature in the range studied.

Four measurements of vapor pressure at 25 °C, two at 3.0 mL/min and two at 8.0 mL/min, were performed to determine whether vapor saturation is established in the saturator chamber, in this range of flow rates. The vapor pressure and corresponding standard deviations were $(2.32 \pm 0.29) \times 10^{-4}$ Pa at 3.0 mL/min and $(2.24 \pm 0.14) \times 10^{-4}$ Pa at 8.0 mL/min. These results verify the saturated conditions and also indicate that recoveries are essentially constant in this range of flow rates.

Table 2 gives the results of vapor pressure at the temperatures studied. These values resulted from four independent measurements at each temperature. The masses of collected triadimefon (between 0.015 and 0.035

Table 2. Mean and Standard Deviations of Vapor Pressure Measurements of Triadimefon

t/°C	p/Pa	t/°C	p/Pa
25	$(2.25 \pm 0.24) \times 10^{-4}$	50	$(8.39 \pm 0.22) \times 10^{-3}$
30	$(5.35 \pm 0.56) \times 10^{-4}$	55	$(1.79 \pm 0.16) \times 10^{-2}$
35	$(1.02 \pm 0.06) \times 10^{-3}$	60	$(2.92 \pm 0.32) \times 10^{-2}$
40	$(2.37 \pm 0.17) \times 10^{-3}$	65	$(5.03 \pm 0.40) \times 10^{-2}$
45	$(4.09 \pm 0.19) \times 10^{-3}$	70	$(8.72 \pm 0.29) \times 10^{-2}$

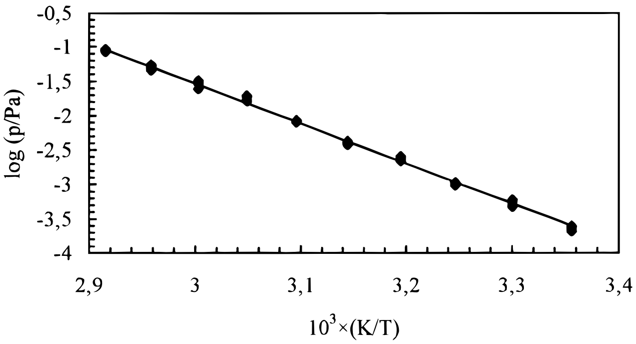

Figure 2. Logarithms of triadimefon vapor pressure as function of the reciprocal of the absolute temperature: (◆) experimental; (—) $\log p/\mathrm{Pa} = (15.87 \pm 0.35) - (5802 \pm 113)K/T$.

mg) in the vapor pressure determinations and recovery studies were similar. The standard deviations are generally around or below 10% of the mean value.

The linear regression of the logarithm of the vapor pressure was calculated by weighted linear least squares as a function of reciprocal temperature using all the data. The regression coefficients A an B were, for 95% confidence, 15.87 ± 0.35 and 5802 ± 113, respectively, and the correlation coefficient was 0.999. The values of $\log p$ as function of $1/T$ and the calculated linear regression curve are plotted in Figure 2. The relationship $\log p$ vs $1/T$ is linear, which means that the enthalpy of sublimation may be considered constant in the range of temperatures studied, despite the proximity of the melting point (82.3 °C). The value of $\Delta_{\mathrm{sub}}H$, calculated from B, is (111.1 ± 2.2) $\mathrm{kJ \cdot mol^{-1}}$.

We have compared our results with the rather unreliable results available in the literature. In their review of pesticide properties, Wauchope *et al.* (1992) cite the values of 1.1×10^{-4} Pa at 20 °C and 2.0×10^{-3} Pa at 40 °C but also mention a value of 2.0×10^{-6} Pa for 20 °C. Tomlin (1994) reports the values of 2×10^{-5} Pa and 6×10^{-5} Pa for 20 °C and 25 °C, respectively. Our results are in excellent agreement with the first two cited by Wauchope *et al.* and are not far away from the values reported by Tomlin.

Conclusions

Accurate vapor pressure measurements have been made for triadimefon between 25 °C and 70 °C. The results presented in this work demonstrate that the method used has no systematic errors and can be applied at least in the range of 30 Pa to 2×10^{-4} Pa with a standard deviation equal to or less than 10%.

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Literature Cited

Ambrose, D. Pressure-Volume-Temperature. In *Recommended Reference Materials for the Realization of Physicochemical Properties*; Marsh, K. N., Ed., Blackwell Scientific Publications: Oxford, U.K., 1987.

Da Silva, J. P.; Da Silva, A. M. Contribution of Volatilization and Photodegradation to the Dissipation of Triadimefon from Solid Waste. *Proceedings of the International Conference on Environmental Pollution*, Barcelona, 1993; Nath, B., Candela, L., Hens, L., Robin, J. P., Eds.; European Centre for Pollution Research, University of London: London, 1993; Vol. 2, pp 533−539.

Kuo, H.-W.; Wang, J.-D.; Lin, J.-M. Determination of Vapor Pressure for 4,4′-Bipyridine by Gas Saturation and Gas Chromatographic Methods. *Chemosphere* **1992**, *25*, 1679−1686.

Macknick, A. B.; Prausnitz, J. M. Vapor Pressures of High-Molecular-Weight Hydrocarbons. *Ind. Eng. Chem. Fundam.* **1979**, 18, 348−351.

Morabito, P. L.; Ormand, J. R.; Nestrick, T. J. Dynamic Vapor Generator for Moderate and Low Volatility Compounds. *Chemosphere* **1990**, *21*, 991−997.

OSHA Analytical Methods Manual, Method 62. Organic Methods Evaluation Branch, OSHA Analytical Laboratory: Salt Lake City, UT, 1986.

OSHA Analytical Methods Manual, Method 63. Organic Methods Evaluation Branch, OSHA Analytical Laboratory: Salt Lake City, UT, 1987a.

OSHA Analytical Methods Manual, Method 67. Organic Methods Evaluation Branch, OSHA Analytical Laboratory: Salt Lake City, UT, 1987b.

OSHA Analytical Methods Manual, Method 70. Organic Methods Evaluation Branch, OSHA Analytical Laboratory: Salt Lake City, UT, 1988a.

OSHA Analytical Methods Manual, Method 74. Organic Methods Evaluation Branch, OSHA Analytical Laboratory: Salt Lake City, UT, 1988b.

Rothman, A. M. Low Vapor Pressure Determination by the Radiotracer Transpiration Method. *J. Agric. Food Chem.* **1980**, *28*, 1225−1228.

Skene, W. G.; Krzymien, M. E. Vapor Pressure of Tri-*n*-butyl Phosphate. *J. Chem. Eng. Data* **1995**, *40*, 394−397.

Sonnefeld, W. J.; Zoller, W. H.; May, W. E. Dynamic Coupled-Column Liquid Chromatographic Determination of Ambient Temperature Vapor Pressures of Polynuclear Aromatic Hydrocarbons. *Anal. Chem.* **1983**, *55*, 275−280.

Spencer, W. F.; Cliath, M. M. Vapor density of dieldrin. *Environ. Sci. Technol.* **1969**, *3*, 670−674.

Spencer, W. F.; Cliath, M. M. Vapor Density and Apparent Vapor Pressure of Lindane (γBHC). *J. Agric. Food Chem.* **1970**, *18*, 529−530.

Spencer, W. F.; Cliath, M. M. Volatility of DDT and related compounds. *J. Agric. Food Chem.* **1972**, *20*, 645−649.

Spencer, W. F.; Cliath, M. M. Measurement of Pesticide Vapor Pressures. *Residue Rev.* **1983**, *85*, 57−71.

Spencer, W. F.; Shoup, T. D.; Cliath, M. M.; Farmer, W. F.; Haque, R. Vapor Pressures and Relative Volatility of Ethyl and Methyl Parathion. *J. Agric. Food Chem.* **1979**, *27*, 273−278.

Thomas, T. C.; Nishioka, Y. A. Sampling of Airborne Pesticides Using Chromosorb 102. *Bull. Environ. Contam. Toxicol.* **1985**, *35*, 460−465.

Tomlin, C., Ed. *The Pesticide Manual, Incorporating The Agrochemicals Handbook*, 10th ed.; British Crop Protection Council: Surrey, U.K., 1994.

Turner, B. C.; Glotfelty, D. E. Field Air Sampling of Pesticide Vapors with Polyurethane Foam. *Anal. Chem.* **1977**, *49*, 7−10.

Wania, F.; Shiu, W. Y.; Mackay, D. Measurement of Vapor Pressure of Several Low-Volatility Organochlorine Chemicals at Low Temperatures with a Gas Saturation Method. *J. Chem. Eng. Data* **1994**, *39*, 572−577.

Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Beckers, P. W.; Burt, J. P. The SCS/ARS/CES Pesticide Properties Database for Environmental Decision-Making, *Rev. Environ. Contam. Toxicol.* **1992**, *123*, 1−155.

Westcott, J. W.; Simon, C. G.; Bidleman, T. F. Determination of Polychlorinated Biphenyl Vapor Pressures by a Semimicro Gas Saturation Method. *Environ. Sci. Technol.* **1981**, *15*, 1375−1378.

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