

GAS CHROMATOGRAPHIC DETERMINATION  
OF SMALL VAPOUR PRESSURES  
DETERMINATION OF THE VAPOUR  
PRESSURES OF SOME TRIAZINE HERBICIDES

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INTRODUCTION

Various trisubstituted symmetrical triazines are used nowadays as herbicides<sup>1-3</sup>. GAST<sup>4</sup> has examined triazines of this kind with respect to their properties as herbicides, and found that even the vapour of these substances had an effect upon plants. In order to obtain information on the amount of herbicide present in the vapour phase, we determined the vapour pressure of 10 different herbicides.

The vapour pressure of substances can be determined in various ways<sup>5,6</sup>, a simple procedure being the gas saturation method<sup>5-7</sup>. A stream of dry inert gas is passed over the substance under examination in such a way that a saturated vapour results, the latter being in equilibrium with the solid phase. The saturation pressure of the substance is represented by its partial vapour pressure. Subsequently, the vapour is condensed, the amount of solid substance is determined by suitable means and the vapour pressure is finally obtained by calculation. For pressures in the order of magnitude of  $10^{-4}$  to  $10^{-5}$  mm Hg, the amount of substance transferred, assuming an average molecular weight of 250, is in the order of  $10^{-6}$  g/l carrier gas. The amount of substance to be transferred depends on the sensitivity of the analytical procedure used. The measurement of vapour pressures of this order requires either a considerable amount of inert gas being passed through the system or, alternatively, a very sensitive method for determining minute quantities of condensed substance. High sensitivities are obtainable with methods like spectrophotometry, mass spectroscopy, etc. For our purpose, we thought gas chromatography with a flame ionisation detector the most suitable method. Gas chromatography is also highly selective and is therefore more advantageous than gravimetric, photometric or other non-specific methods. The substances to be examined is not required in an absolutely pure form. Any small impurities with a relatively higher vapour pressure do not cause an incorrect partial vapour pressure since the desired compound is obtained selectively in its pure form by gas chromatographic separation.

It will be shown later in this report that a simultaneous determination of the vapour pressures of several substances is possible without detrimental mutual interference. A further advantage consists in the fact that by using a gas chromatographic technique, the time-consuming degassing of the substance, in order to remove interfering substances which have relatively high vapour pressure, is unnecessary.

## PRINCIPLE

The stream of gas leaving the saturation column 6 (Fig. 1) is fed to a gas chromatographic column 7, the latter being packed with a stationary phase suitable for the substance to be examined. Column 7 is cooled by solid carbon dioxide; the triazine therefore condenses. The total amount of gas passed through the system is obtained by measurement of the volume of water being forced from the gasometer. The substance condensed in column 7 is subsequently eluted in the gas chromatograph at a given temperature.

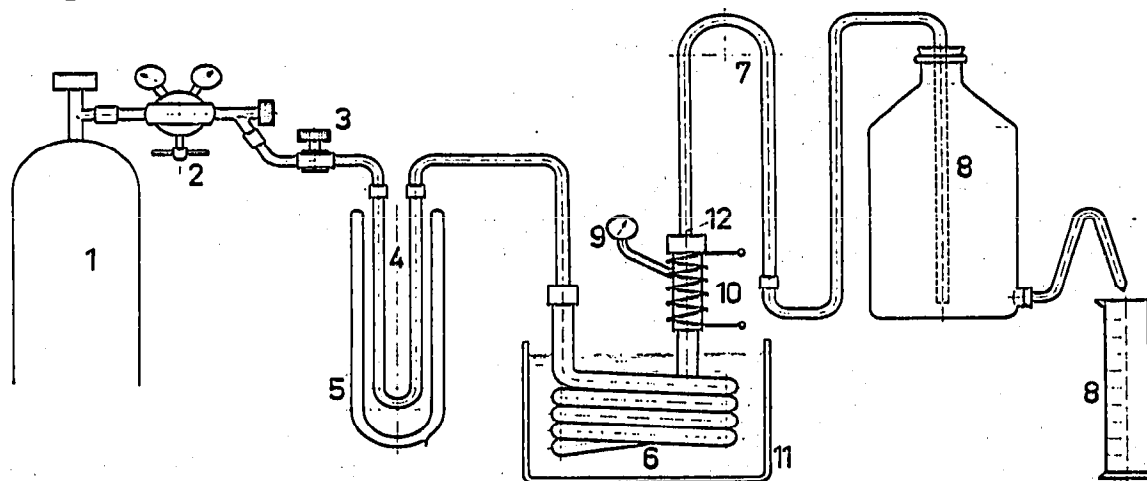


Fig. 1. Scheme of the apparatus. 1 = Nitrogen cylinder; 2 = pressure valve; 3 = fine adjustment of pressure; 4 = drying column packed with 5 Å molecular sieve; 5 = Dewar flask; 6 = saturation column; 7 = absorption column; 8 = measurement of the volume of inert gas; 9 = pressure at the outlet of the saturation column; 10 = heating between the saturation column and the gas chromatographic column; 11 = constant temperature bath; 12 = condensation of the transferred substance by means of dry ice.

If the total amount of gas used ( $V$ ), the condensed amount of vapour ( $m$ ), the molecular weight ( $M$ ) and the experimental temperature ( $T$ ) are known, the saturation pressure ( $p_s$ ) is calculated by equation (1):

$$p_s = \frac{m}{M} \cdot \frac{22.415}{V_c} \cdot \frac{T}{273} \cdot \frac{p_B}{p_C} \cdot p_B \quad (1)$$

where  $p_s$  = saturation pressure (mm Hg),

$m$  = weight of transported substance (g),

$M$  = molecular weight of substance,

$V_c$  = volume of inert gas, as measured at the outlet of the gas chromatographic column (ml),

$T$  = absolute temperature of the saturation column,

$p_B$  = pressure of the inert gas at the outlet of the saturation column (mm Hg),

$p_C$  = pressure of the inert gas at the outlet of the absorption column (mm Hg).

The ratio  $p_B/p_C$  corrects the gas volume at the outlet of the absorption column to that at the outlet of the saturation column. The *conditio sine qua non* for the application of the saturation method is the total saturation of the vapour leaving the column. This can easily be checked by carrying out a test series with the same compound at

varying gas flow rates. It can be shown that in a packed column having a pressure drop, a continuous saturation of the carrier gas from the inlet to the outlet takes place (Fig. 2). Due to the pressure drop between point A and B of the saturation column and between point B and C of the absorption column, the inert gas continually expands ( $V_C > V_B > V_A$  if  $p_C < p_B < p_A$ ). In order to establish the equilibrium, continuous

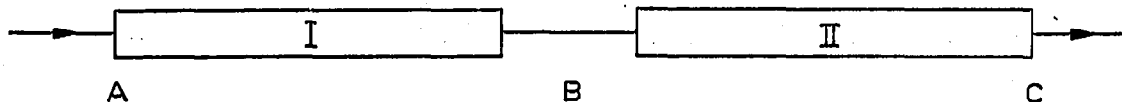


Fig. 2. I = Saturation column; II = absorption column (gas chromatographic column); A = inlet of inert gas; B = passage between I and II; C = outlet of the absorption column (point of integral measurement of the volume of the carrier gas at atmospheric pressure).

vaporisation throughout the saturation column is necessary. There is a further pressure gradient between point B and C in the absorption column (7), but no more solid is available here. The volume of carrier gas measured at point C ( $V_C$ ) is compressed to  $V_B$  at point B:

$$V_B = V_C \cdot \frac{p_C}{p_B}$$

The volume of gas measured at point C has to be corrected for the conditions existing at point B because no further equilibrium between vapour and solid occurs during the absorption in the gas chromatographic column.

#### EXPERIMENTAL

##### *Apparatus (see Fig. 1)*

Pure nitrogen (99.99 %) is used as the transport gas. Traces of moisture are removed by passing the gas through a 5 Å molecular sieve column (4), which is cooled by solid carbon dioxide (5). The dried gas is now led into the saturation column (6), the latter consisting of a stainless steel tube of 2 m length and having an internal diameter of 8 mm. The column is packed with a mechanical mixture of 1 part of triazine and 6 parts of celite (20/30 mesh). The addition of celite increases the surface and improves the permeability of the column. Experiments showed that the same values for the vapour pressure were obtained whether the column had been packed with a mixture of triazines and celite or whether the solid phase had been impregnated with the triazines dissolved in a suitable solvent. The saturation column is plugged at each end by means of glass wool. A Haake-Ultra-Thermostat (11) maintains the desired temperature of the column to within  $\pm 0.2^\circ$ . The outlet (10) of the saturation column above the heating bath is electrically heated in order to avoid condensation of the volatile material in this part of the column. This heating equipment consists of a 100 W-cartridge heater, its output being controlled by a Variac (Fig. 3). The chromatographic column (7) extends a few mm into this heated zone from above. The column is joined to the saturation column by means of Ermeto tube-fittings so as to make the junction air tight. The condensation of the triazines in the gas chromatographic column is effected 5 cm above the level of the tube connection by cooling (9) with solid carbon dioxide.

A gas chromatographic column of 1 m in length and 4 mm I.D. packed with

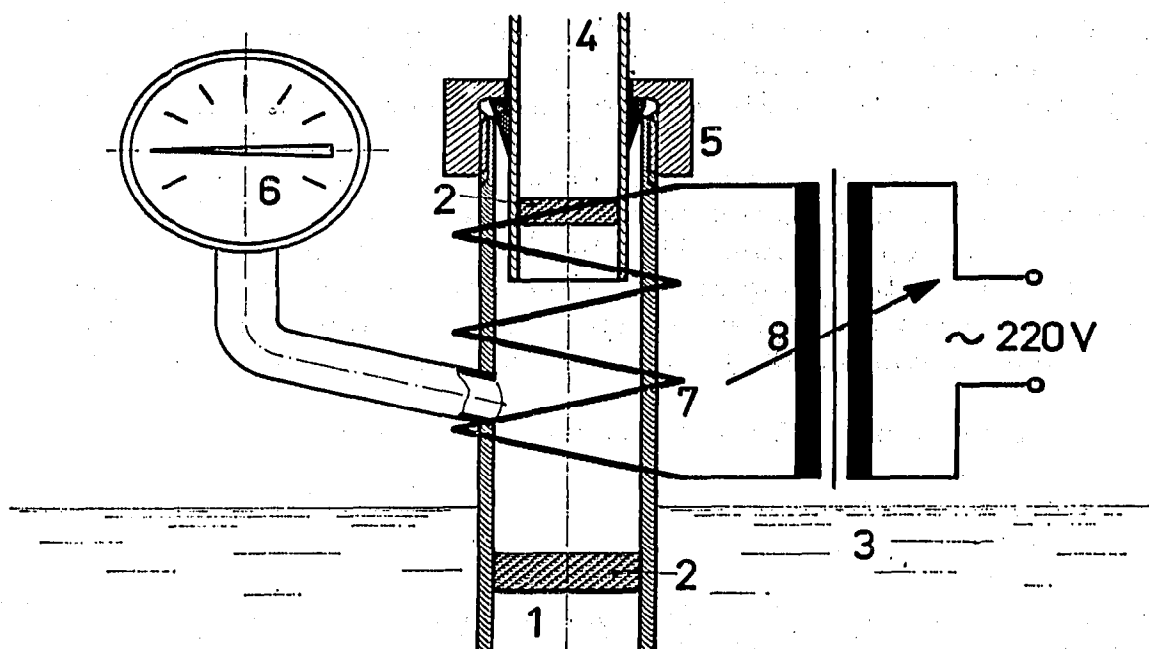


Fig. 3. Detail of tube connections. 1 = Saturation column; 2 = glass wool plugs; 3 = constant temperature bath; 4 = absorption column (gas chromatographic column); 5 = Ermeto tube fittings; 6 = pressure gauge 0-0.15 atm; 7 = heating 100 V; 8 = Variac.

1% Reoplex 400 on kieselguhr (40/60 mesh) is very suitable for the absorption and the subsequent separation of the triazines. The determination is finally completed by disconnecting the chromatographic column from the saturation column and putting the former into the gas chromatograph. The type used in our laboratory was Perkin-Elmer, Fraktometer 116 E, equipped with flame ionization detector.

#### Working conditions

*Pre-conditioning of the saturation column.* This may be achieved before the substance is transferred to the absorption column, in order to remove the more volatile impurities. The necessity for pre-conditioning the substance under examination depends on the purity, volatility and possibility of interference in gas chromatographic determination. As an example, although this is not generally necessary, a column charged with Prometryne [2-methylmercapto-4,6-bis-(isopropylamino)-s-triazine] was pre-conditioned for 16 h at 130° and at a flow rate of 50 ml/min. The other triazines, even as mixtures, may be conditioned in a similar way.

*Selection of flow rate.* By altering the gas flow rate, one can ascertain whether the gas stream is completely saturated with the vapour of the substance under investigation. It is known that high flow rates result in incomplete saturation of the gas as the amount of substance transported is too small. Our experiments on the triazine herbicides showed saturation over a wide range of flow rates. Although the experiments discussed in this paper were carried out at a flow rate of 25 ml/min, doubling this value still did not lead to a decrease in transported substance.

*Procedure.* The cooled gas chromatographic column is connected to the saturation column for a given time, the total amount of carrier gas depending on the vapour pressure. Normally it is sufficient to transport 0.2-50 µg of triazine. Thereupon the gas chromatographic column is disconnected from the saturation apparatus and 10 µl

of a suitable standard are injected into the former by means of a Hamilton syringe. The triazine peaks and the standard peak on the chart should be of the same order of magnitude, this being achieved by selecting the proper concentration of the standard solution.

Other related triazines which differed completely from the peaks of the triazines in the mixture under investigation were chosen as standards. The correction factors were determined in separate runs. The absorption column is now placed in the gas chromatograph, the latter being already heated to the separation temperature. The flow rate of the carrier gas is then adjusted and the chromatogram is recorded. The chromatographic separation of the various triazines was made under the following conditions:

Column: 1 m, 4 mm I.D., 1 % Reoplex 400 on kieselguhr (acid washed 40/60 mesh),

Separating temperature: 180°,

Carrier gas: Nitrogen,

Flow rate: 30 ml/min,

Duration: 10 to 40 min, depending on the triazine examined.

The peak areas of the standard and sample are determined by planimetry and the total amount of transferred substance is calculated from the figures of the standard added, correction factor and peak areas.

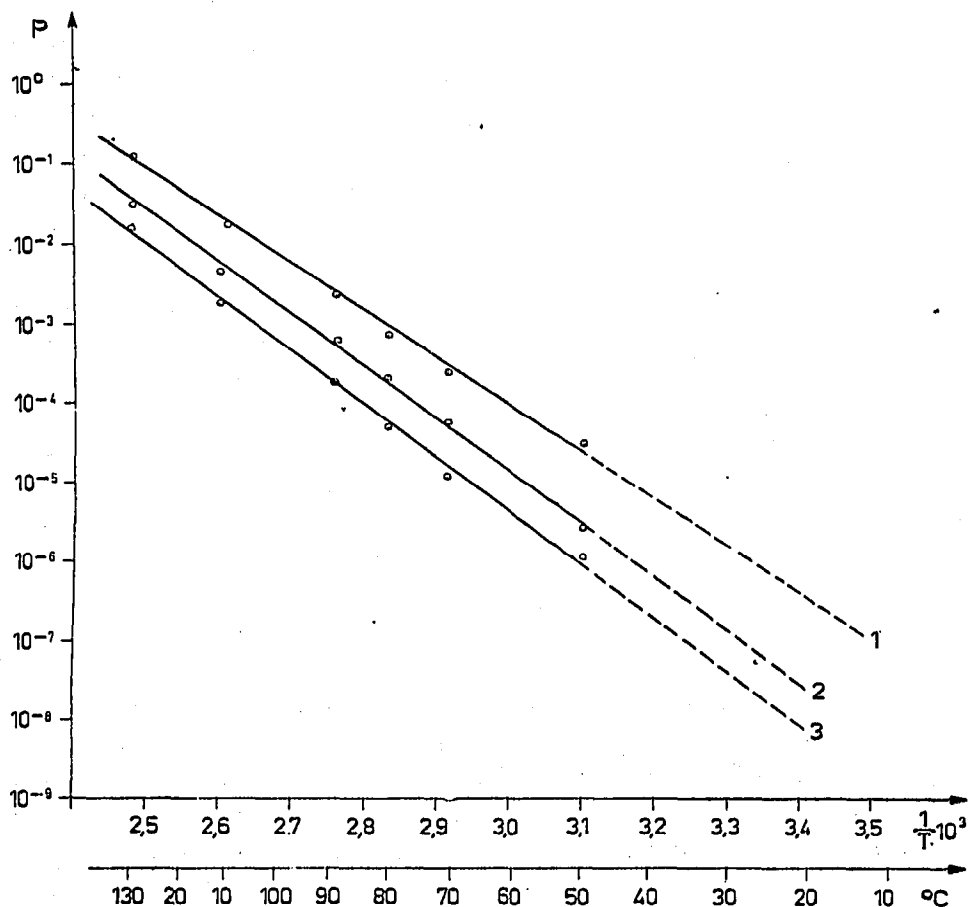


Fig. 4. Vapour pressure diagrams of 3 triazine herbicides. 1 = Atrazine; 2 = Propazine; 3 = Simazine.

## RESULTS AND DISCUSSION

The vapour pressures of 10 triazines were determined in the range of 50° to 130° and the data are expressed by means of the vapour pressure constants  $A$  and  $B$  of the equation (2)

$$\log p = A - \frac{B}{T} \quad (2)$$

which is derived<sup>7</sup> from the Clausius-Clapeyron equation (3)

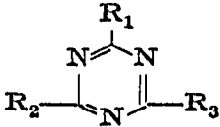
$$\frac{d \ln p}{d (1/T)} = - \frac{\Delta H}{R} \quad (3)$$

where  $A$  and  $B$  = vapour pressure constants,  
 $T$  = absolute temperature,  
 $\Delta H$  = heat of vaporization per mole,  
 $R$  = gas constant.

In Fig. 4, the vapour pressures obtained experimentally are plotted against the reciprocal absolute temperature for Azatrine, Propazine and Simazine. The straight lines indicate that eqn. (2) is quite accurate. The values for the vapour pressure constants of ten different triazines are given in Table I. The last column contains the vapour pressure extrapolated to 20°.

A considerable saving of time was achieved by the simultaneous determination of the vapour pressures of several triazines. The purity of the triazines under investigation ranged between 95–100%. None of the impurities present had a detrimental effect on the results. By using a flame ionisation detector, only minute quanti-

TABLE I  
 VAPOUR PRESSURES AND VAPOUR PRESSURE CONSTANTS OF TEN SUBSTITUTED SYMMETRICAL TRIAZINES

Name	$R_1$	$R_2$	$R_3$	$A^*$	$B^*$	$P_{\text{mm Hg}}^{**}$ (293° K)
						
Atrazine	-Cl	-NHC <sub>2</sub> H <sub>5</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	13.766	5945	3.0 · 10 <sup>-7</sup>
Propazine	-Cl	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	14.754	6533	2.9 · 10 <sup>-8</sup>
Simazine	-Cl	-NHC <sub>2</sub> H <sub>5</sub>	-NHC <sub>2</sub> H <sub>5</sub>	15.107	6833	6.1 · 10 <sup>-9</sup>
Atratone	-OCH <sub>3</sub>	-NHC <sub>2</sub> H <sub>5</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	11.303	4933	2.9 · 10 <sup>-6</sup>
Prometone	-OCH <sub>3</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	10.794	4817	2.3 · 10 <sup>-6</sup>
Simetone	-OCH <sub>3</sub>	-NHC <sub>2</sub> H <sub>5</sub>	-NHC <sub>2</sub> H <sub>5</sub>	11.894	5130	2.4 · 10 <sup>-6</sup>
Ametryne	-SCH <sub>3</sub>	-NHC <sub>2</sub> H <sub>5</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	11.911	5270	8.4 · 10 <sup>-7</sup>
Prometryne	-SCH <sub>3</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	-NH- <i>i</i> -C <sub>3</sub> H <sub>7</sub>	11.841	5222	1.0 · 10 <sup>-6</sup>
Simetryne	-SCH <sub>3</sub>	-NHC <sub>2</sub> H <sub>5</sub>	-NHC <sub>2</sub> H <sub>5</sub>	11.914	5293	7.1 · 10 <sup>-7</sup>
GS 34360	-SCH <sub>3</sub>	-NHCH <sub>3</sub>	-NHCH(CH <sub>3</sub> ) <sub>2</sub>	12.101	5302	1.0 · 10 <sup>-6</sup>

\*  $A$  and  $B$  = vapour pressure constants (see ref. 6).

\*\*  $P_{\text{mm Hg}}$  = vapour pressures at 293° K, calculated by eqn. (2).

ties of transferred substance are required for one determination and the transition time is low. On the other hand the determination of very low vapour pressures is achieved by using a minimum amount of transfer gas.

#### SUMMARY

A new method for the determination of vapour pressures by means of gas chromatography is described. A stream of inert gas is passed through a saturation column and the transferred substance is condensed in a cooled gas chromatographic column. A solution of a suitable standard is injected into the column and the condensed substance is subsequently eluted in a gas chromatograph at a preselected temperature. Vapour pressures in the order of  $10^{-5}$  to  $10^{-6}$  mm Hg can easily be determined. Ten 1,3,5-triazines substituted in the 2,4,6-positions were investigated in the temperature range of  $50^{\circ}$  to  $130^{\circ}$ , the vapour pressure constants were calculated and the extrapolated figures of the vapour pressures at  $20^{\circ}$  are given.

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