MOLECULAR WEIGHT DETERMINATION WITH THE MARTIN DENSITY BALANCE

C. S. G. PHILLIPS AND P. L. TIMMS*

Inorganic Chemistry Laboratory, Oxford (Great Britain)

A frequent problem in gas-chromatography is the identification of compounds giving rise to peaks on the chromatogram, when they cannot be characterised by their retention times. The gas-density balance, designed by MARTIN[1] for use as a gas-chromatographic detector, gives a response which is a simple function of the densities of the carrier gas and vapours which pass through it, and so it can be used to determine the molecular weights of small amounts of vapours as an aid to their identification.

When a weight q of a vapour of molecular weight M is passed through the density balance in a stream of carrier gas, molecular weight m, an integral response (normally the peak area) A is obtained at constant flow rate such that

$$q = kA \frac{M}{M - m} \tag{1}$$

where k is a constant for a particular instrument. LIBERTI et al.[2] have determined molecular weights with the balance by measuring its change in response to a vapour in the presence of carrier gases of different molecular weights. By injecting separate portions of the same mixture of volatile compounds, containing one compound of known molecular weight, on to a chromatographic column before the balance, two sets of responses are obtained, so that

$$\frac{A}{A_1} \frac{M_1 - m}{M - m} = \frac{A'}{A_1'} \frac{M_1 - m'}{M - m'} \tag{2}$$

where M and M_1 are the molecular weights for the known and unknown compounds, m and m' are the molecular weights of the carrier gases, and A, A' and A_1, A_1' are the peak areas with the two carrier gases of the known and unknown compound. The method is very attractive in that it allows the molecular weights of all the peaks in a chromatogram to be determined without prior separation, provided that the molecular weight of one is known. LIBERTI et al. claimed an accuracy of 4 % in their molecular weight determinations. From our own experience we are able to substantiate this claim, but we have found that there are a number of difficulties which are not immediately apparent in the method. In the first place the calculation is such that small percentage errors in peak areas become considerably magnified in the final

---

* Present address, Borax Consolidated Limited, Chessington, Surrey.

molecular weight. Secondly it is essential that the ratio of the two components (unknown and known molecular weights) in the two portions used with different carrier gases should be constant to within 1%. This may be obtained by injection with a microsyringe, the method used by LIBERTI et al., but it is necessary to flush out the needle of the syringe with some of the sample immediately before injection. Capillary injection[3] and stream splitting devices in which the sample was divided into two in the gas phase were not found to provide adequate reproducibility. The latter was found to be within $\pm 2\%$ in most cases, and molecular weight determinations correspondingly ± 5 to 10%, using an average of about four determinations for each mixture.

We have therefore developed an alternative method for finding molecular weights with the density balance. Equation (1) can be arranged to

$$q/M = kA/(M - m)$$

or

$$PV = KA/(M - m) \tag{3}$$

where P and V are the pressure and volume of a vapour, and K a new constant. Thus by making pressure-volume measurements on a vapour and then passing it through the density balance, the molecular weight M can be found. Unlike LIBERTI's method, pure vapours are required, but these are readily obtained from a mixture in sufficient amounts by gas–liquid chromatography. The constant K in equation (3) is evaluated with a compound of known molecular weight.

EXPERIMENTAL

The density balance was a copper-block instrument constructed by Dr. A. J. P. MARTIN (Abbotsbury Laboratories, Elstree, Herts). Whenever possible it was used at room temperature, when it is about twice as sensitive as it is at $100°$. The electrical response from the balance was fed to a 2 mV Honeywell-Brown potentiometric recorder. A transmitting slidewire on the recorder could be used to operate an electrical integrator (proportional counter motor) for peak area measurements, but this was found less accurate and reliable than cutting out the peaks from the recorder chart paper and weighing them.

The Pressure-Volume apparatus measured pressure at almost constant volume. Fig. 1 shows one form (Apparatus I), incorporating a PEARSON manometer[4] and designed so that both it and the density balance were operated at room temperature. A small correction was made for the variation in sensitivity of the balance with variation in room temperature. The whole apparatus could be evacuated, the connecting tubes between T_1 and T_3 all being of 4 mm bore, which gave a reasonable compromise between a low dead volume and a high pumping speed. The trap B was constructed of quill-tubing. The vapour contained in the volume E (110 ml) could be isolated from the rest of the system by means of the mercury cut-off C. The widening of the tube in this cut-off at the Y-junction made it possible to open the cut-off

satisfactorily (by withdrawing mercury through the tap) even when there was a small pressure difference across it.
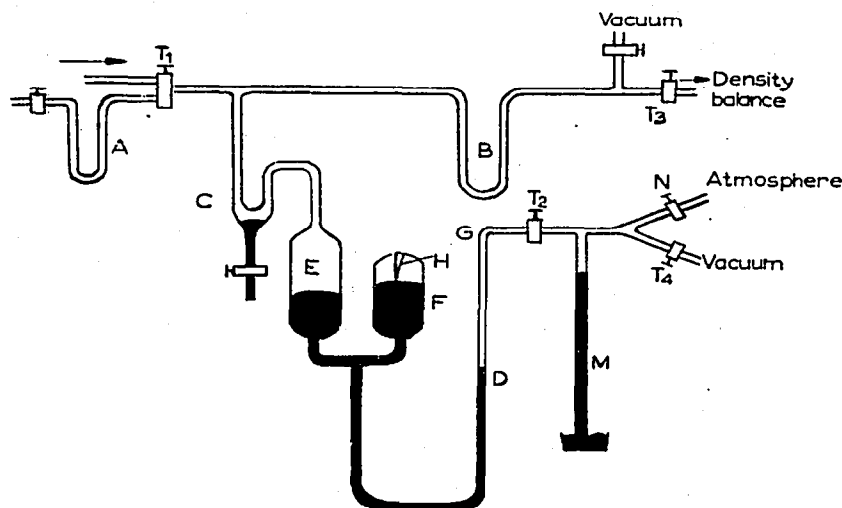

Fig. 1. The Pressure-Volume system (Apparatus I).

The operating procedure was as follows:

(1) The sample (which might correspond with a chromatogram peak) was trapped in A at liquid air temperature. The whole of the Pressure-Volume system was evacuated, a rotary oil-pump being found quite sufficient for this purpose. The sample was allowed to evaporate slowly from A until its pressure in the system (as measured roughly by the depression of the mercury in E) was sufficient. T_1 was then closed and A recooled to retain the rest of the sample.

(2) B was now cooled in liquid air, and after one to two minutes the system evacuated again. This indirect transfer from A to B has been found essential in order to displace adsorbed non-condensible gas from the walls of the system[5]. If this procedure was not adopted, very slow transfer from E to B occurred when the sample was finally retrapped into B (see paragraph (6) below).

(3) By operation of T_4, connected to vacuum, air was withdrawn from G, thus lowering the mercury level F below the pointer H. Operation of the needle valve N (connected to atmosphere) now allowed the mercury to be raised slowly in F until it just touched H. The mercury level in the precision-bore tubing D was now read. This cycle of operations (paragraph (3)) was repeated until a constant value of the mercury level in D was obtained.

(4) The sample in B was allowed to warm up and fill E. The valve C was closed and the rest of the system thoroughly evacuated (in our apparatus this involved approximately 10 % of the sample in B being run to waste).

(5) By repeating the operations in paragraph (3), a new reading of the mercury level in D was obtained. The difference between this reading and the previous reading was equal to the pressure of the vapour in E multiplied by the ratio

cross-sectional area of E/cross-sectional area of D,

which was 55 in our apparatus. The pressures measured were normally 1–6 mm of mercury, corresponding to about 5–30 cm movement in D.

The volume of vapour in E varies very slightly with its pressure, the correction from constant volume being of the order of 1%. (For measurements above room temperature when D was inside a vapour jacket it was found more convenient to measure the movement of the mercury in D as a change in pressure of the gas in G, registered on the manometer M.)

(6) B was cooled in liquid air and the vapour transferred to it from E by opening C. Transfer normally took about 20 min, and was checked for completeness by measuring the vacuum in E as in paragraph (3) above.

(7) Tap T_2 was closed and nitrogen (or other carrier gas) was introduced slowly (otherwise the top of F is shattered) into the system through T_1. (Tap T_2 may be replaced by a tap in the narrow tube immediately below E. Less care is then necessary as F and G are protected, but small errors can arise from tap-grease rising in the mercury into E.) A flow of nitrogen through T_3 into the density balance was then established, and when the flow and the electrical output from the balance were steady, the gas flow was measured and the sample introduced by allowing B to warm up. The flow was checked after the sample had passed through the balance. A soap-film flow-meter, accuracy $\pm$ 0.5%, was used.

(The tube connecting T_3 to the density balance may contain conveniently a gas–liquid chromatographic column. This has the advantage that if the sample contains some impurity then this is detected and allowance made. If T_3 is connected directly to the density balance, then B must only be allowed to warm up slowly so that a sufficiently spread-out "peak" is obtained on the recorder.)

The room-temperature apparatus has been found satisfactory for substances with boiling points up to 150°. For higher boiling substances, it was necessary to raise the temperature of the Pressure-Volume system in order to produce sufficiently high vapour pressures. Measurements have been made with the Pearson manometer (E, F and D) and the density balance maintained at 100° with a steam-jacket, and with the connecting tubes electrically heated above this temperature (Apparatus II). In this case each of the unheated taps was protected by mercury cut-offs similar to C. T_3 was warmed for the passage of the sample into the density balance. At 100° loss of mercury from the Pearson manometer by distillation becomes a serious factor. It was reduced by keeping C at 100° and closed as much as possible.

For compounds boiling below 90°, the Pearson manometer may be replaced by a bulb of about 10 ml capacity, the vapour pressures of such compounds at room-temperature being sufficient for them to be measured accurately by a simple mano-meter (Apparatus III).

RESULTS AND DISCUSSION

Table I shows results obtained with various forms of the Pressure-Volume apparatus. The values of the determined molecular weights are mostly the averages of two or three measurements with each compound. The maximum errors in the individual

determinations were 1.5 % for Apparatus I and II and 1.9 % for Apparatus III.

The constant K (equation (3)) was determined using benzene for Apparatus I and III, and chlorobenzene in Apparatus II. The standard deviations for seven of these calibration runs with each apparatus were 0.7 %, 1.0 % and 1.7 % for Apparatus I, II and III respectively.

TABLE I

MOLECULAR WEIGHT DETERMINATIONS

Compound	Boiling point °C	Molecular weight	Determined molecular weight	Error %
Apparatus I				
Diethyl ether	35	74.1	74.0	—0.1
Ethyl propionate	99	102.1	102.2	+0.1
Toluene	110	92.1	92.6	+0.5
p-Xylene	138	106.2	107.1	+0.8
Tetrachloroethane	146 .	167.9	168.0	+0.1
Silicon tetrachloride	58	169.9	170.9	+0.6
Trisilane	53	92.3	92.4	+0.1
Tetrasilane	ca. 108	122.4	122.2	—0.2
Apparatus II				
Mesitylene	165	120.2	120.1	—0.1
Dimethylaniline	193	121.2	120.8	+0.5
Apparatus III				
Ethyl bromide	38	109.0	108.3	—0.6
Methyl ethyl ketone	80	72.1	72.4	+0.4
Trichloroethylene	87	131.4	131.2	—0.2

A total of 1 to 6 mg of each compound was used to measure the molecular weights given for Apparatus I and II and slightly more for Apparatus III. With Apparatus I and II, the quantity used could readily be reduced by a factor of 10 by suitable amplification of the density-balance response (the noise level is low enough for this to be possible) and reduction of the volume of E. About 1 h was required for a single molecular weight determination with Apparatus I and II, but only 35 to 40 min with Apparatus III as this was simpler to operate.

Compounds with boiling points greater than 200° have not been determined successfully with Apparatus II, although this was designed for compounds boiling up to 250°. In experiments with higher boiling compounds the measured molecular weights were too high, probably due to inadequate heating of the apparatus and significant adsorption of the compounds in the Pressure-Volume system.

The initial measurements of the molecular weights of the silanes and silicon tetrachloride using Apparatus I gave low results. In each case, however, after four measurements the molecular weight had risen to the expected value. This effect was traced to decomposition of part of the silane or of silicon tetrachloride by reaction with the internal surface of the density balance. Once the surface had been conditioned by exposure to the appropriate vapour, all the sample from the Pressure-Volume

system could pass through the balance without reaction. When traces of moisture or air were allowed into the balance the conditioning was destroyed and low molecular weight results obtained. This defect has been overcome by the use of a glass density balance[7]. There was no decomposition of the reactive compounds in the Pressure-Volume apparatus.

SUMMARY

Vapour samples, which may be trapped out from a gas-chromatographic analysis, are measured in a Pressure-Volume apparatus and weighed in a Martin gas-density balance. Molecular weights may thus be determined to an accuracy of better than 1 %.

REFERENCES

1 A. J. P. MARTIN AND A. T. JAMES, *Biochem. J.*, 63 (1956) 138.
2 A. LIBERTI, L. CONTI AND V. CRESCENZI, *Nature*, 178 (1956) 1067; *Atti accad. nazl. Lincei, Rend. Classe sci. fis. mat. e nat.*, 20 (1956) 623.
3 R. P. W. SCOTT, in D. H. DESTY, *Vapour Phase Chromatography*, Butterworths, London, 1957, p. 131.
4 T. G. PEARSON, *Z. physik. Chem.*, 156 (1931) 86.
5 B. LAMBERT AND C. S. G. PHILLIPS, *Phil. Trans. Roy. Soc. London*, A 242 (1950) 415.
6 K. BORER AND C. S. G. PHILLIPS, *Proc. Chem. Soc.*, (1959) 189.
7 J. G. HAMLIN, Part II, *Thesis*, Oxford University, 1960.