

## Notes

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### A new gas chromatographic method for molecular weight determinations using a gas density detector

As the signal of a gas density detector depends on the density of gas flowing through it, its performance can be used for determination of the molecular weight of compounds eluted from a chromatographic column. LIBERTI *et al.*<sup>1</sup> have determined the molecular weights of the components of a sample by adding an external standard to it and using two carrier gases, nitrogen and argon. The error in the determination of molecular weight by this method was estimated at a level of 3–5 % (refs. 1–3). PARSONS<sup>4</sup> obtained much better accuracy by means of the so-called bracket method, choosing for each component one carrier gas of lower molecular weight and one of higher molecular weight than that of the component to be determined. By applying a very sophisticated procedure PHILLIPS AND TIMMS<sup>5</sup> reduced the error of the determination of the molecular weight as low as 1 %.

In this paper, determination of the molecular weights of sample components based on the previously described linear relationship method<sup>6,7</sup> is reported.

#### *Experimental*

*Apparatus.* The instrument used in this study was a laboratory-constructed gas chromatograph with a Gow-Mac Model 091 gas density detector and a Siemens 0–2.5 mV recorder. A U-shaped copper column of 2 m length  $\times$  4 mm I.D. packed with 15 % polyethylene glycol on Chromosorb W (45–60 mesh) was used. The operating conditions were: column temperature, 100°; injector temperature, 120°; carrier gas, nitrogen; reference flow rate, 70 ml/min; sample flow rate, 30 ml/min; detector current, 100 mA; sample size, 0.5  $\mu$ l.

*Materials.* Pure ethyl ether was obtained from Chemical Works "Pronit", acetone A.R. grade from Chemical Works Oświęcim, and absolute ethanol 99.8 %, *n*-propanol for chromatography, and isobutanol for chromatography from Spirit Works Łódź.

*Sampling.* Ethyl ether, acetone, ethanol and *n*-propanol were mixed together in various volume proportions. Ten mixtures were obtained in this way. A known amount of standard (isobutanol) was added to each accurately weighed mixture. Each such sample was injected into the chromatograph three times. The peak areas were determined as the products of their height and half-height width and are reported in Table I.

*Procedure.* According to Procedure 1 (ref. 6) the following equation can be written:

TABLE I  
WEIGHTS OF SAMPLES AND STANDARDS AND PEAK AREAS

Sample no.	In-jection	Weight of mixture, $m$ (g)	Weight of standard, $m_s$ (g)	Areas of peak, $P_i$ (cm <sup>2</sup> ) of				Areas of peak of standard, $P_s$ (cm <sup>2</sup> )
				Ethyl ether	Acetone	Ethanol	n-Pro-panol	
1	a	3.0928	1.6028	7.17	7.14	5.04	7.30	16.0
	b			8.09	7.84	5.47	8.27	17.5
	c			8.48	8.36	5.96	9.02	19.6
2	a	2.7796	1.6001	7.48	3.54	1.41	1.01	8.96
	b			7.81	3.77	1.44	1.16	10.0
	c			7.93	3.79	1.52	0.96	9.41
3	a	2.9353	1.5972	1.69	13.3	5.3	4.26	17.1
	b			1.77	14.9	5.82	4.49	18.9
	c			0.76	6.74	2.56	1.89	8.68
4	a	2.9233	1.6260	4.16	1.74	10.6	7.45	15.6
	b			4.12	1.87	11.5	8.70	19.0
	c			3.69	1.59	10.8	8.13	18.2
5	a	2.8912	1.6090	8.42	4.07	1.50	16.7	19.3
	b			7.75	3.70	1.23	15.8	17.8
	c			7.87	3.75	1.32	15.7	17.9
6	a	3.7874	1.6568	7.30	6.87	1.25	1.80	8.18
	b			6.65	6.49	1.24	1.94	8.28
	c			5.91	5.71	1.05	1.67	7.54
7	a	3.9865	1.6239	3.47	3.37	9.20	13.4	15.1
	b			3.32	3.25	9.02	12.7	14.3
	c			3.24	3.34	9.28	14.0	15.4
8	a	3.9540	1.5961	3.51	12.5	9.90	3.93	15.4
	b			3.69	13.3	10.3	3.72	16.0
	c			1.74	6.19	4.62	1.72	7.32
9	a	3.8032	1.6115	6.54	1.50	4.84	1.98	8.22
	b			7.67	1.77	5.42	2.15	8.69
	c			6.95	1.62	4.86	1.86	7.75
10	a	3.4108	1.6036	7.02	1.68	2.47	3.84	8.20
	b			6.51	1.52	1.90	3.80	8.31
	c			6.78	1.64	2.40	3.58	7.74

$$\sum_{i=1}^4 k_{is} P_i = \frac{m}{m_s} P_s \quad (1)$$

where  $k_{is}$  is the area factor of component  $i$  relative to the area factor of the standard  $s$ ;  $P_i$  and  $P_s$  are the peak areas of the  $i$ -component and standard, respectively; and  $m$  and  $m_s$  are the weights of the sample and standard, respectively.

The area factor of the  $i$ -component may be expressed by the formula:

$$k_i = \frac{M_i}{M_i - M_c} \quad (2)$$

where  $M_i$  is the molecular weight of the  $i$ -component and  $M_c$  is the molecular weight of carrier gas.

As the exact value of the standard area factor  $k_s$  can be calculated from formula 2 the data obtained can be expressed in the form:

$$\sum_{i=1}^4 k_i P_i = \frac{m}{m_s} k_s P_s \quad (3)$$

The area factors  $k_i$  have been estimated by the least squares procedure from a set of thirty such equations, and the molecular weights of all four components have been calculated according to formula 2 (Table II).

The standard errors (s.e.) of the area factors  $k_i$  were found according to the formula<sup>8</sup>:

$$s.e.(k_i) = \sqrt{(s^2 \cdot c_{ii})} \quad (4)$$

where  $s^2$  is the residual sum of squares divided by the residual degrees of freedom,  $c_{ii}$  is diagonal element of a variance-covariance matrix.

#### Results and discussion

The molecular weights of components (Table II) determined by this method differ from the true ones by about 2-4 units, that is by about 3-5 %. It is worth noting that the standard error of area factors for all components is of the same order,

TABLE II

AREA FACTORS AND THE MOLECULAR WEIGHTS OF VARIOUS COMPONENTS OF MIXTURES

Component	Calculated area factor, $k_i$	Standard error of $k_i$	Calculated mol. wt. $M_{ic}$	True mol. wt. $M_i$	$M_{ic} - M_i$	Standard error of $M_{ic}$
Ethyl ether	1.662	0.0783	70.2	74	- 3.8	5.00
Acetone	1.984	0.0684	56.4	58	- 1.6	1.97
Ethanol	2.425	0.0821	47.6	46	+ 1.6	1.13
n-Propanol	1.796	0.0633	63.2	60	+ 3.2	2.80

but the standard error of molecular weight determination depends very much on the difference between the molecular weight of a given component and that of the carrier gas. This is because both these values are related by the formula:

$$s.e.(M_{ic}) = s.e.(k_i) \frac{[M_{ic} - M_c]^2}{M_c} \quad (5)$$

This is also confirmed by our data for ethyl ether, the standard deviation from the true value being 5 units (mol. wt. 74.) and for ethanol, 1 unit (mol. wt. 46).

It seems that molecular weight determination by the proposed method is at least as accurate as by other reported methods<sup>1-3</sup>. The greatest advantage of this method is that it is easy to perform, as only one carrier gas is used. Reliable results

may be achieved providing that the molecular weight of the carrier gas is not too far away from the molecular weights of the components being determined.

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*Institute of Heavy Organic Synthesis,  
Blachownia Sl. (Poland)*

J. HETPER  
A. JANIK

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