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### Determination of dead times for inverse gas chromatography: measurements by use of methane

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The determination of dead times in gas chromatographic (GC) systems has frequently been discussed and there are several reviews dealing with this problem<sup>1–7</sup>. If chromatographs equipped with flame ionization detectors are applied, the simplest method for measuring the dead time consists in the use of methane as a marker<sup>8</sup>, but this may be the source of significant errors. Therefore, its importance is doubtful and its applicability is at least considerably limited. There is no doubt that methane shows marked adsorption at lower temperatures. Ettre<sup>9</sup> reported errors when methane was used below 70°C, and Garcia Dominguez *et al.*<sup>10</sup> found that methane should be retained by normal liquid phases at temperatures as high as 180°C. Guberska<sup>11,12</sup> proposed an empirical equation for adjusting the measured dead time, considering the amount of stationary phase in the column but not any dependence on temperature. However, we found such a dependence and we therefore propose a simple method for eliminating or at least strongly reducing the errors due to methane adsorption.

#### EXPERIMENTAL

A Varian 3700 GC apparatus equipped with a flame ionization detector and a Chromatron Model 18.3-4 chromatograph equipped with a thermal conductivity detector were used. The carrier gases were nitrogen and hydrogen, respectively. Methane or air was injected in doses of 1  $\mu$ l for the flame ionization detector and 5  $\mu$ l for the thermal conductivity detector using a Hamilton syringe. The retention time was measured manually with a stopwatch and in addition as far as possible electronically using a Varian CDS-111 instrument. All reported times are averages of at least five measurements. The stationary phases, Carbowax 20M in the thermal conductivity measurements and a polymer such as polyurethane, was coated on 60–80-mesh Chromosorb W AW by dissolution in chloroform and slow evaporation using a rotary evaporator. After drying and rescreening, the coated support was packed into 2-m stainless-steel columns of 2 or 3 mm O.D.

## RESULTS AND DISCUSSION

The retention times of methane and air were measured at a constant carrier gas flow-rate depending on the temperature used. The data are given in Table I together with the inlet pressures, the James-Martin factors and the adjusted dead times. For the mode of adjustment, see below.

TABLE I

## COMPARISON OF DETECTION TIMES OF METHANE AND AIR WITH CALCULATED VALUES

Column, 5% Carbowax 20M on Chromosorb W AW (60-80 mesh); hydrogen flow-rate, 12.28 ml/min;  $P_0 = 752$  mmHg.

$T$ (K)	$t_{CH_4}$ (s)	$P_i$ (mmHg)	$j$	$t_{adj.}$ (s)	$t_{air}$ (s)
313.2	23.8	1230	0.744	22.07	22.2
323.2	23.2	1241	0.740	21.95	22.0
333.2	22.7	1253	0.735	21.80	21.8
343.2	22.3	1268	0.730	21.65	21.6
353.2	21.9	1275	0.726	21.53	21.6
363.2	21.7	1286	0.722	21.42	21.4
373.2	21.4	1298	0.717	21.27	21.3
383.2	21.1	1308	0.713	21.15	21.1
393.2	21.0	1318	0.709	21.03	21.0
403.2	21.0	1328	0.705	20.91	20.9
413.2	20.8	1343	0.699	20.73	20.7
423.2	20.6	1358	0.694	20.59	20.6
433.2	20.4	1371	0.689	20.44	20.4
433.2	20.3	1381	0.685	20.32	20.3
453.2	20.2	1395	0.681	20.2	20.2

It can be seen that methane is retained distinctly longer than air at temperatures below 120°C, which agrees with the findings of Wainwright *et al.*<sup>13</sup>. Therefore, methane seems to be suitable for dead time determinations under limited conditions.

However, in inverse GC the real retention time of methane is of less interest than the real retention times of the carrier gas used. At variable temperatures these retention times depend primarily on pressure. At a constant carrier gas flow-rate the inlet pressure ( $P_i$ ) increases with increasing temperature. The average column pressure ( $\bar{P}$ ) changes in a corresponding manner. In calculating the retention volumes, these effects are usually taken account by introducing the James-Martin factor,  $j$ :

$$j = \frac{P_0}{\bar{P}} \cdot \frac{3[(P_i/P_0)^2 - 1]}{2[(P_i/P_0)^3 - 1]}$$

Therefore, it seemed to be evident that in order to calculate dead time at lower pressure drops along the column and at lower temperatures on the basis of mea-

TABLE II

## COMPARISON OF METHANE DETECTION TIMES AND CALCULATED DEAD TIMES

Column 1: 10% polyurethane on Chromosorb W AW (60–80 mesh); nitrogen flow-rate, 10.91 ml/min;  $P_0 = 754.5$  mmHg. Column 2: 10% polyoxypropylene on Chromosorb W AW (60–80 mesh); nitrogen flow-rate, 11.27 ml/min;  $P_0 = 761$  mmHg.

$T$ (K)	Column 1				Column 2			
	$t_{CH_4}$ (s)	$P_i$ (mmHg)	$j$	$t_{adj.}$ (s)	$t_{CH_4}$ (s)	$P_i$ (mmHg)	$j$	$t_{adj.}$ (s)
313.2	52.2	1096	0.806	49.37	29.4	1316	0.716	27.41
323.2	51.3	1103	0.803	49.19	28.5	1332	0.710	27.18
333.2	50.5	1109	0.800	49.00	28.2	1348	0.703	26.91
343.2	49.8	1119	0.796	48.76	27.9	1367	0.696	26.64
353.2	49.4	1126	0.792	48.52	27.3	1387	0.689	26.37
363.2	48.7	1136	0.788	48.27	26.7	1408	0.682	26.10
373.2	48.3	1144	0.784	48.02	26.2	1427	0.675	25.84
383.2	47.9	1151	0.780	47.78	25.8	1450	0.667	25.53
393.2	47.6	1162	0.776	47.54	25.3	1472	0.659	25.22
403.2	47.3	1169	0.772	47.29	25.0	1494	0.652	24.96
413.2	47.0	1179	0.768	47.04	24.6	1518	0.644	24.65
423.2	46.8	1188	0.764	46.8	24.3	1545	0.636	24.34
433.2	—	—	—	—	24.0	1572	0.627	24.0

measurements with methane at higher temperatures ( $T_1 \geq 120^\circ\text{C}$ ), it is necessary to consider these factors. The adjustment consists in multiplying the dead time measured at  $T_1$  with the quotient of the James–Martin factors at both temperatures. It stands to reason that any possible difference in the flow-rate must be considered in a similar manner. The corresponding data for two of the investigated polymers are given in Table II, but without a comparison with air retention due to the use of a flame ionization detector. Methane is increasingly retained at decreasing temperatures; the correlation of the measured and calculated values at temperatures above  $120^\circ\text{C}$  is excellent. Even at temperatures between 70 and  $120^\circ\text{C}$  the measured values do not differ appreciably from the calculated values, provided that the carrier gas flow-rate is increased to such an extent that the system cannot reach distribution equilibrium.

In general, we can say that methane is not adsorbed and therefore can be used without correction for dead time determinations if the values measured under two sets of conditions [temperature, flow-rate ( $F$ ) and resulting pressure],  $C_1$  and  $C_2$ , fit the following equation:

$$t_{CH_4C_2} = t_{CH_4C_1} \cdot \frac{F_{C_1}}{F_{C_2}} \cdot \frac{j_{C_2}}{j_{C_1}}$$

In the same way, it is possible to calculate the dead time under methane adsorption conditions ( $C_2$ ) from those without adsorption ( $C_1$ ). The applicability of this equation could also be observed by using adjusted values in thermodynamic calculations, for instance in determining the  $\chi$  parameters of interaction. These results will be published in a future paper.

## REFERENCES

- 1 R. Kaiser, *Chromatographia*, 2 (1969) 215.
- 2 J. K. Haken, M. S. Wainwright and R. J. Smith, *J. Chromatogr.*, 133 (1977) 1.
- 3 J. Ševčík and M. S. H. Löwentap, *J. Chromatogr.*, 147 (1978) 75.
- 4 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 147 (1978) 65.
- 5 L. S. Ettre, *Chromatographia*, 13 (1980) 73.
- 6 M. S. Wainwright and J. K. Haken, *J. Chromatogr.*, 184 (1980) 1.
- 7 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 334 (1985) 95.
- 8 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
- 9 L. S. Ettre, *Chromatographia*, 6 (1973) 489.
- 10 J. A. Garcia Dominguez, J. Garcia Munoz, E. Fernandez Sanchez and M. J. Molera, *J. Chromatogr. Sci.*, 15 (1977) 520.
- 11 J. Guberska, *Chem. Anal. (Warsaw)*, 18 (1973) 1059.
- 12 J. Guberska, *Chem. Anal. (Warsaw)*, 19 (1974) 161.
- 13 M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 188 (1980) 246.