CHROM. 9099

Letter to the Editor

Effect of column temperature on the sensitivity of katharometer response

Sir,

In a paper published recently[1] in this journal, we discussed the effect of the column temperature on the sensitivity of katharometer response; this work was presented at the symposium *Advances in Chromatography 1975*, in Munich, where it gave rise to much controversy. This letter is intended to justify the views of the opponents and to provide further comments on the subject.

The idea described in the paper was based on the relationship $A_i = Cf_i n_i RT/Pv$, where A_i, n_i, f_i, R and C are, respectively, the peak area, the number of moles of solute component i, the molar response factor, the perfect-gas constant, and an apparatus constant, and T, P and v are the absolute temperature, the pressure and the volume flow-rate of the column effluent at the outlet. The above relationship shows that the peak area corresponding to a given amount of solute substance will increase in proportion to the column temperature, provided that all the other parameters are kept constant. In order to verify this concept, peak areas corresponding to equal charges of solute chromatographed at different column temperatures and constant carrier-gas mass flow-rate were measured. This experimental model is, unfortunately, inconsistent with the above theory, as P, T and v are interdependent if the mass flow-rate is constant. Hence, the theory and the experiment by themselves were correct, but their relationship was wrong.

In accordance with objections raised at the symposium, the peak area indeed should not be affected by the column temperature at a constant mass flow-rate of carrier gas; in fact, it was altered almost as much as theory would predict for the case of constant volume flow-rate of carrier gas. This situation led us to repeat the measurements using a different instrument, but the results were similar to those obtained earlier[1]. The instrument and the working conditions were as follows: an F & M (Avondale, Pa., U.S.A.) Model 810 gas chromatograph equipped with a separately thermostatted four-filament katharometer (bridge current 190 mA), 180 cm × 4.5 mm I.D. stainless-steel columns packed with (i) 25 % of Apiezon L or (ii) 25 % of hexadecane on Chromosorb W (60–80 mesh), or with (iii) a combined packing consisting of lengths of 160 cm of packing (ii) and 20 cm of packing (i) in series. The carrier gas was hydrogen. In all measurements at constant mass flow-rate of carrier-gas, the flow-rate was maintained at 1 ml/sec as measured at 745 Torr and 25°C (ambient conditions), the katharometer body being thermostatted at 185°C. In measurement at constant volume flow-rate [column (i) only], the flow-rate measured at 745 Torr and 298°K ($v_{745,298}$) was varied so as to keep the product $v_{745,298} \times T$ constant, and the temperature of the katharometer body was always set equal to the column temperature. The effect of the katharometer temperature on the sensitivity was measured independently and was found to be insignificant (see Table I). In the isothermal GC runs, 5-μl

TABLE I

EFFECT OF KATHAROMETER TEMPERATURE ON PEAK AREA

Column temperature 70°C; Apiezon L; hydrogen at constant mass flow-rate.

Detector temperature (°C)	Peak area (counts)
60	382
80	382
100	377
120	381
150	393
180	386
200	383

charges of a solution (99 mg/ml) of n-octane in chloroform were injected at a sensitivity setting of 1/16 throughout; a Hamilton Type 701 Nsyringe (Hamilton, Bonaduz, Switzerland) was used for the injections. The chromatograms were recorded with a Hewlett-Packard Model 7128A recorder (Pasadena, Calif., U.S.A.) and integrated with a Disc integrator (Disc Instruments, Santa Ana, Calif., U.S.A.). The volume flow-rate was measured with a home-made high-precision capillary flowmeter. The precision of all the controls and measurements was better than 1 %. The isothermal experiments were carried out at two column temperatures (T_1, T_2), and the results are summarized in Table II. It can be seen that, with the Apiezon L column and constant mass flow-rate [case (i)], the ratio $A_t(T_2)/A_t(T_1)$ is smaller than the corresponding ratio of T_2/T_1, whereas with the same column operated at constant volume flow-rate [case (i)*], the situation is reversed. With the hexadecane column and constant mass flow-rate [case (ii)], the sensitivity-reducing effect of stationary-phase bleeding[2] can again be observed; this effect is eliminated by trapping the hexadecane vapour in the layer of Apiezon L packing [case (iii)].

TABLE II

EFFECT OF COLUMN TEMPERATURE ON PEAK AREA

GC column	T_1 (°K)	T_2 (°K)	$A_t(T_1)$ (counts)	$A_t(T_2)$ (counts)	$\dfrac{T_2}{T_1}$	$\dfrac{A_t(T_2)}{A_t(T_1)}$
i	343	393	400	436	1.15	1.09
i*	343	395	374	460	1.15	1.23
ii	343	377	408	409	1.10	1.00
iii	346	379	398	423	1.10	1.06

* Constant volume flow-rate.

The increase in A_t with increase in T is also apparent in temperature programming; Table III shows the results of normalizing the peak areas of pentane and mesitylene chromatographed both isothermally and at different temperature rates on the Apiezon L column at constant mass flow-rate [conditions (i)].

The dependence of A_t on T at constant mass flow-rate was not caused by change in this flow-rate[3]. At each column temperature, the flow-rate measured at ambient

TABLE III

EFFECT OF TEMPERATURE PROGRAMMING ON PEAK-AREA FRACTION CALCULAT-
ED BY NORMALISATION

GC conditions	Area (%)		T_{ret} (°C)		Error (%)	
	Pentane	Mesitylene	Pentane	Mesitylene	Pentane	Mesitylene
Isothermal (120°C)	48.1	51.9	—	—	—	—
Programmed temp.* (6°C/min)	43.4	56.6	74	175	−9.77	9.06
Programmed temp.* (10°C/min)	42.2	57.8	82	196	−12.3	11.4
Programmed temp.* (20°C/min)	41.5	58.5	106	240	−13.7	12.7

* Initial temperature 60°C.

values of T and P was practically constant. The same situation obtained under condi-
tions of temperature programming; the temperature-induced variation in the hold-up
of a mass of gas in the column[4] had practically no effect on the volume flow-rate as
measured at the detector-cell outlet. This is probably attributable to the fact that the
effect of increasing the absolute mean pressure of the gas in the column is counteracted
by that of increasing the temperature of the gas. In addition, the column used [cf.
case (i)] showed a small pneumatic resistance (column-inlet excess pressures of only
0.375 and 0.655 Torr at 50° and 200°C, respectively, with a hydrogen flow-rate of
1 ml/sec at 298°K and 745 Torr).

The results indicate that the effect of T on A_i is more involved, i.e., in addition
to the effect discussed in the theoretical section of the original paper[1], there must be
some effect that makes the peak area detected by a thermal-conductivity detector
dependent on T also at constant mass flow-rate of carrier gas. The physical substance
of this finding is unknown to us and we do not wish to generalize about it; the peak
area may also be independent of T with some other experimental arrangements.
Nevertheless, reproduction of the phenomenon with a different instrument shows that
this phenomenon may occur commonly, with all the practical implications stated
previously[1], especially with regard to quantitative analysis by programmed-temper-
ature GC with thermal-conductivity detection.

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