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EFFECT OF COLUMN TEMPERATURE ON THE SENSITIVITY OF KATHAROMETER RESPONSE

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SUMMARY

The katharometer is a concentration-sensitive detector that responds to the mole fraction of the solute component in the column effluent. For a given amount of solute introduced into the gas chromatographic (GC) column and chromatographed under constant operating conditions, the peak area is proportional to the absolute column temperature. In quantitative programmed-temperature GC with the use of the internal normalization technique, the peak areas can approximately be corrected by dividing them by the corresponding absolute retention temperatures. The dependence of the peak area on column temperature may be compensated for by the decrease in the net response due to the background response brought about by column bleeding.

INTRODUCTION

The katharometer is one of the most thoroughly studied gas chromatographic (GC) detectors. Owing to its great versatility, it has become a standard accessory with modern commercial analytical gas chromatographs. A detailed description of the individual variants, design and performance characteristics of the katharometer was given by Jentzsch and Otte[1].

Despite its being one of the oldest detectors, it still provides a source of interesting problems and attracts the attention of chromatographers. A number of papers have dealt with the prediction[2–8] and/or determination[9–12] of katharometer response factors. Some peculiar properties of the katharometer as a GC detector were described by Bohemen and Purnell[13]. Hawkes and Wheaton[14] found that the pressure of the carrier gas was an important factor in detection with the katharometer. The object of the present work was to establish the dependence of the integral katharometer response on the column temperature. This rather unexpected phenomenon stems, in a similar manner to the phenomenon studied by Hawkes and Wheaton-from the fact that the katharometer is a special type of concentration-sensitive detector, responding to the relative concentration of the solute component in the column effluent[15].

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THEORETICAL

Situation in the detector

The instantaneous net response of the katharometer to a component i, R_i, can be defined as the difference between the temperatures that the filament in the measuring cell displays when the cell is fed with a solute vapour–carrier gas mixture and with the carrier gas alone, T_{i0} and T_0, respectively, *i.e.*,

$$R_i = T_{i0} - T_0 \tag{1}$$

Assuming that the Joule heat produced in the filament is dissipated by heat conduction only, *i.e.*, neglecting heat dissipation by convection, radiation and spurious conduction via electrical wiring, we can write for a cylindrical hot-wire cell with a coaxially situated filament the equations

$$T_{i0} - T_c = q\,[\ln (r_c/r_f)]/2\pi L k_{i0} \tag{2}$$

and

$$T_0 - T_c = q\,[\ln (r_c/r_f)]/2\pi L k_0 \tag{3}$$

where T_c is the temperature of the inner wall of the cell, q is the heat produced in the filament, r_c and r_f are the diameters of the cell and of the filament, respectively, L is the length of the cell and k_{i0} and k_0 are the thermal conductivity coefficients of the solute vapour–carrier gas mixture and of the carrier gas, respectively. Eqns. 2 and 3 are valid provided that the heat capacity of the filament and the gas within the cell is negligible compared with that of the katharometer block. Eqns. 1–3 give

$$R_i = q \cdot \frac{\ln (r_c/r_f)}{2\pi L} \left(\frac{1}{k_{i0}} - \frac{1}{k_0}\right) \tag{4}$$

Expanding T_{i0} into a Taylor series about k_{i0}, considering only the first two terms of the series, and assuming that k_{i0} approaches k_0 under usual GC conditions, we obtain

$$R_i = -q \cdot \frac{\ln (r_c/r_f)}{2\pi L k_0^2} (k_{i0} - k_0) \tag{5}$$

The quantity k_{i0} is a function of the concentration of the solute component in the column effluent. According to the Wassiljewa equation[16],

$$k_{i0} = \frac{k_i}{1 + A_{0i}(y_0/y_i)} + \frac{k_0}{1 + A_{i0}(y_i/y_0)} \tag{6}$$

where k_i is the thermal conductivity coefficient of the solute vapour alone, y_i and y_0 are the mole fractions of solute vapour and carrier gas in the solute vapour–carrier gas mixture and A_{0i} and A_{i0} are constants defined by

$$A_{i0} = [(\sigma_i + \sigma_0)/2\sigma_0]^2\,[(M_i + M_0)/2M_i]^{\frac{1}{2}}$$

and

$$A_{0i} = [(\sigma_i + \sigma_0)/2\sigma_i]^2\,[(M_i + M_0)/2M_0]^{\frac{1}{2}}$$

where σ and M are the effective molecular collision diameters and molecular weights of solute i and carrier gas 0, respectively. Substituting $1 - y_i$ for y_0, expanding k_{i0} into a McLaurin series about y_i, and again taking into account the first two terms only, eqn. 6 becomes

$$k_{i0} = k_0 + [(k_i/A_{0i}) - k_0 A_{i0}]\, y_i \tag{7}$$

and the combination of eqns. 5 and 7 gives

$$R_i = -q \cdot \frac{\ln (r_c/r_f)}{2\pi L k_0^2} \left(\frac{k_i}{A_{0i}} - k_0 A_{i0}\right) y_i \tag{8}$$

It is apparent from eqn. 8 that the katharometer is a concentration-sensitive detector, the net response of which is proportional to the mole fraction of solute i in the column effluent, *i.e.*, to the relative solute concentration.

Situation in the column

Let us consider a GC zone migrating down the column, produced by the slug injection of n_i moles of component i. Under the conditions of linear chromatography, the number of moles of component i present in the mobile phase, n_{im}, is $n_{im} = n_i/(1 + k)$ throughout the column, where k is the capacity ratio. At a distance z of the centre of the zone from the column inlet, the mean concentration of component i, $\bar{c}_{iz}$, in the mobile phase within the zone is

$$\bar{c}_{iz} = n_{im}/\Delta V_z = n_i/\Delta V_z\,(1 + k) \tag{9}$$

where ΔV_z is the volume of the gas within the zone. At the distance z, the velocity at the centre of the zone, u_{iz}, is related to the velocity of the mobile phase, u_z, by the equation $u_{iz} = u_z/(1 + k)$. As the quantity ΔV_z can be expressed by $\Delta V_z = \varnothing u_{iz} \Delta t_z$, where $\varnothing$ is the cross-sectional area occupied by the mobile phase and Δt_z is the time interval between the beginning and the end of the passage of the zone through the cross-section at the distance z, eqn. 9 can be re-written as $\bar{c}_{iz} = n_i/\varnothing \Delta t_z u_z$. When considering the situation at the column outlet, we can omit the subscripts z and write

$$\bar{c}_i = n_i/\varnothing \Delta t u = n_i/v\Delta t \tag{10}$$

where u and v are the forward and volume flow-velocities of the carrier gas as measured at the column outlet, respectively, and Δt is the time interval between the beginning and the end of elution of the zone from the column. The mean solute concentration at the column outlet can further be expressed formally as

$$\bar{c}_i = \frac{1}{\Delta t} \int_{t_1}^{t_2} c_i\,(t)\, \mathrm{d}t \tag{11}$$

where $c_i\,(t)$ is the instantaneous solute concentration in the effluent at the column outlet and t_1 and t_2 are the times of the beginning and the end of elution of the zone, respectively ($\Delta t = t_2 - t_1$), and the combination of eqns. 10 and 11 gives

$$\int_{t_1}^{t_2} c_i\,(t)\, \mathrm{d}t = \frac{n_i}{v} \tag{12}$$

Hence the chromatographic zone is described in terms of the absolute concentration of the solute component.

Relationship between the peak area and the total amount of solute

The area of the chromatographic peak of component i, A_i, is generally proportional to the time integral of the instantaneous detector response, *i.e.*,

$$A_i \approx \int_{t_1}^{t_2} R_i(t)\,dt \tag{13}$$

In the case of the katharometer, we can write with regard to eqn. 5:

$$A_i = Cq \cdot \frac{\ln(r_c/r_f)}{2\pi L k_0^2}\left(\frac{k_i}{A_{0i}} - k_0 A_{i0}\right)\int_{t_1}^{t_2} y_i(t)\,dt \tag{14}$$

where C is an apparatus constant. In order to match eqns. 14 and 12, c_i in eqn. 12 will be expressed in terms of y_i, *i.e.*,

$$\int_{t_1}^{t_2} y_i(t)\,dt = \frac{n_i}{v}\cdot\frac{RT}{P} \tag{15}$$

where R is the perfect gas constant and T, P and v are the absolute temperature, pressure and volume flow-rate at the column outlet, so that we obtain

$$A_i = Cq \cdot \frac{\ln(r_c/r_f)}{2\pi L k_0^2}\left(\frac{k_i}{A_{0i}} - k_0 A_{i0}\right)\frac{RT}{Pv}\cdot n_i \tag{16}$$

In the context of this assay, it is important to note that T in eqns. 15 and 16 represents the column temperature; in other words, for a given charge of the solute component, the temperature of the katharometer block and all other conditions being kept constant, the peak area will be proportional to the column temperature. Thus, if charges n_{i1} and n_{i2} of component i are chromatographed at absolute column temperatures T_1 and T_2, the corresponding ratio of the peak areas, A_{i1}/A_{i2}, will be

$$\frac{A_{i1}}{A_{i2}} = \frac{n_{i1}}{n_{i2}}\cdot\frac{T_1}{T_2} \tag{17}$$

Eqn. 16 also shows that the katharometer response will be inversely proportional to the pressure of the carrier gas, which is in agreement with the results of Hawkes and Wheaton[14].

EXPERIMENTAL

The concept outlined above was verified experimentally by chromatographing equal charges of a model sample at different column temperatures while keeping the temperature of the katharometer block, the carrier gas flow-rate and the other conditions constant, and correlating the peak areas in the chromatograms so obtained with the corresponding column temperatures. In order to reproduce in this assay the phenomenon of a decrease in the net response on increasing the background response due to column bleeding[17], which was studied with a flame ionization detector, two

different stationary phases were used, one of which was virtually non-volatile and the other showed a considerable volatility under the column temperatures employed.

The model sample was a 0.0984 g/ml solution of *n*-octane (VEB Laboratory Chemicals, Apolda, G.D.R.) in chloroform (Lachema, Brno, Czechoslovakia). The stationary phases employed were Apiezon K (AEI, Manchester, Great Britain) and hexadecane (BDH, Poole, Great Britain), deposited in amounts of 20% (w/w) on Chromosorb W, 60–80 mesh (Carlo Erba, Milan, Italy).

The GC measurements were carried out on a Chrom 4 gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia), equipped with a thermostatted hot-wire katharometer with diffusion cells and operated in the dual-column mode.

With both stationary phases, 1 m × 3 mm I.D. stainless-steel columns were employed; identical columns were installed in both the measuring and the reference channels. Hydrogen was used as the carrier gas; in the measuring channel, the flow-rate was 9.6 ml/min as measured with a soap-bubble flow meter at the detector outlet (24°, 750 mmHg) in both instances. An arbitrary flow-rate was set in the reference channel. The columns were operated at temperatures of 70, 80, 90, 100, 110 and 120° while maintaining the temperature of the detector at 185°. The bridge current was 130 mA. Stabilized sources of a constant mass flow of the carrier gas were installed ahead of the columns in both channels, so that the flow-rate of the gas through the detector cells was assumed to be virtually independent of the changes in the column temperature. This was checked by measuring the flow-rate at the detector outlet at 70 and 120°.

The sample charges were introduced with a Hamilton 701N (10-μl) syringe (Micromesure, The Hague, The Netherlands). After each injection, the correction for the sample volume discharged from the needle was carried out (the volume to be added to the reading on the barrel amounted to about 0.35 μl). Three injections were carried out at each temperature.

The peak areas were determined planimetrically. The detector sensitivity setting and the recorder chart speed were adjusted so as to obtain easy-to-measure peaks; the results were reduced to a standard sensitivity and chart speed.

RESULTS AND DISCUSSION

The peak areas determined for equal sample charges at different column temperatures were referred to the peak area determined at the lowest temperature employed [$A_i(T)/A_i(343)$ and $A_i(T)/A_i(353)$ with Apiezon and hexadecane, respectively] and compared with the corresponding theoretical values ($T/343$ and $T/353$) predictable from eqn. 17. The results are summarized in Table I. It can be seen that with Apiezon K, the relative peak areas follow the corresponding ratios of temperatures closely. With hexadecane, the situation is different; at lower temperatures, the curve of the dependence of peak area on temperature rises slightly, but, upon increasing the column temperature further, this rise falls off and, after reaching a maximum, the curve starts to slope downwards. The temperature dependence of the peak area, as specified by eqns. 16 and 17, actually applies in this case also, but is compensated for by a decrease in the net response due to column bleeding. Provided that the responses to solute and stationary-phase vapour are additive (which is not the case with the katharometer), this decrease is defined by $A_i \approx (f_i - f_b y_b)n_i$, where f_i and f_b are the response factors of component i and of the stationary phase vapour

TABLE I

EXPERIMENTAL RESULTS AND THEORETICAL PREDICTIONS FOR THE DEPENDENCE OF THE PEAK AREA ON THE COLUMN TEMPERATURE

t_R = Retention time.

Column temperature (°C)	*Apiezon K*			*Hexadecane*		
	t_R *(sec)*	$A_l\,(T)$ / $A_l\,(343)$	$\frac{T}{343}$	t_R *(sec)*	$A_l\,(T)$ / $A_l\,(353)$	$\frac{T}{353}$
70	672	1.00	1.000	—	—	—
80	468	1.04	1.039	1071	1.00	1.000
90	326	1.06	1.058	716	1.01	1.038
100	241	1.09	1.087	513	1.01	1.057
110	187	1.12	1.117	361	1.00	1.085
120	146	1.15	1.146	250	0.99	1.113

bled out of the column, respectively, and y_b is the mole fraction of the stationary phase vapour in the column effluent. Hexadecane is volatile and therefore, owing to an exponential increase in the vapour pressure of liquids on increasing the temperature, the negative effect of the column bleeding at first attenuates the increase in the peak area and, at higher column temperatures, it eventually becomes dominant.

With both the Apiezon and hexadecane columns, the peak areas were recorded within a region of fairly linear response. Fig. 1 shows the plots of peak area *versus* sample charge obtained with the Apiezon K (APK) and hexadecane (HD) columns at 120° under identical conditions; a smaller slope of the HD line is again due to the

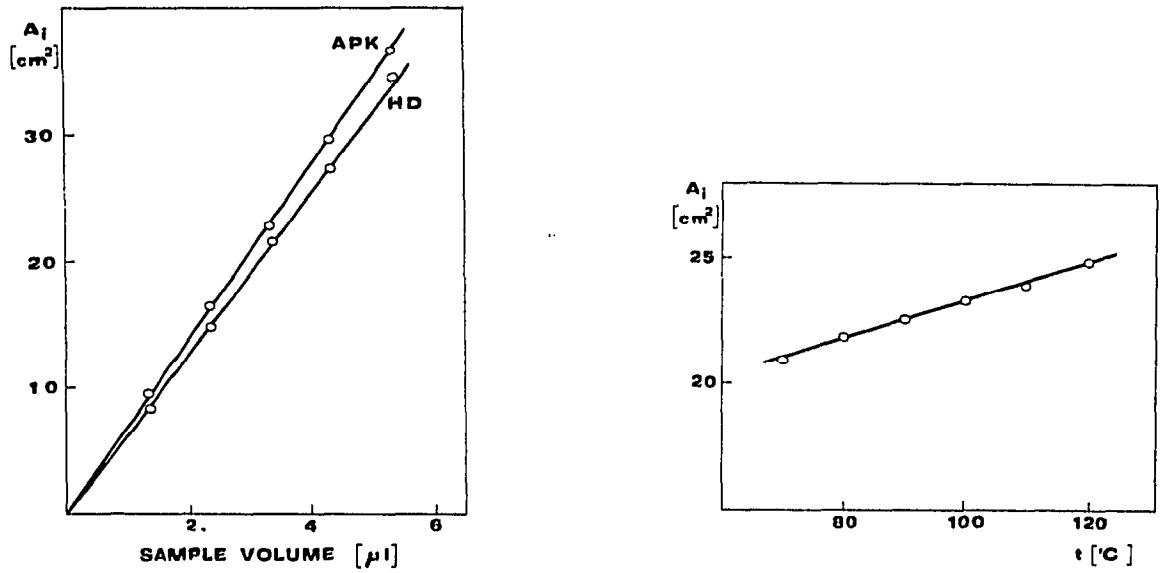

Fig. 1. Peak area *versus* sample charge plots obtained from data measured on Apiezon K (APK) and hexadecane (HD) columns at 120°.

Fig. 2. Peak area *versus* column temperature plot obtained from data measured on the Apiezon K column for a constant sample charge (4 μl) at a constant katharometer temperature (185°).

above effect of the background response. The actual rise of the peak area upon increasing the temperature of the Apiezon K column is shown in Fig. 2.

CONCLUSIONS

(1) A calibration graph obtained by plotting peak areas against sample charges is readily applicable only if the actual analysis is carried out at a column temperature the same as that employed in calibration. Fitting areas obtained from chromatograms run at higher column temperatures leads to positive errors and *vice versa*.

(2) In programmed-temperature gas chromatography (PTGC), the method of normalization of peak areas uncorrected for the column temperature effect described may give erroneous results.

(3) The systematic errors incidental to the dependence of the sensitivity of katharometer response, as outlined under (1) and (2), can be corrected approximately by dividing the peak areas by the actual absolute column temperature; in PTGC, the retention temperatures are applicable in this respect.

(4) With relatively volatile sorbents, the enhancement of the sensitivity of the katharometer response due to an increase in the column temperature may be compensated for by the opposite effect incidental to the background response.

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