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OPTIMIZED FLOW PROGRAMMING FOR TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHY

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SUMMARY

A flow-rate optimization system for gas chromatography is described for use with temperature programming. Carrier gas flow is controlled by feedback electronics and a microcomputer using empirically derived flow optima *vs.* temperature relations. Carrier flow-rate is monitored by a mass-flow meter and adjusted by a microcomputer according to a specified temperature *vs.* flow-rate format. Improvements in theoretical plate heights are shown for this system and results are compared to conventional temperature programming.

INTRODUCTION

Flow programming in gas chromatography (GC) has been used as an alternative to temperature programming to separate analytes with significantly different capacity factors[1–3]. When studying thermally labile samples, flow programming has the advantage that analytes may be separated at lower temperatures.

Exponential increases of carrier gas flow-rates are usually employed in flow programming[1,3–5]; isothermal retention times of a homologous series can be shown to be an exponential function of the carbon number when the eluent flow-rate is constant[4]. Therefore, a linear dependence between carbon number and retention time may be achieved if isothermal carrier flow-rate is increased exponentially[6].

Use of concurrent flow and temperature programming has been demonstrated with capillary columns[1,3,4]. These procedures decrease analysis times and help alleviate bleeding of the stationary phase by effecting separation and elution at lower temperatures. Also, improved separations were attained[1,3]. In flow-programmed systems the inlet column pressure[1,3,5,6] has usualy been controlled; the commercially-available DANI system is an example of a pressure-controlled flow programmer[4]. A mass-flow control system which uses pressure sensors has been evaluated by Wičar[7].

In the work described herein, GC carrier flow-rate is controlled via a flow-feedback system. Height equivalent to theoretical plate (HETP) *vs.* flow plots at different temperatures, and their respective flow-rate optima, were used to establish an optimum flow *vs.* temperature relation. This correspondence was then used to select and regulate carrier flow during temperature-programmed separations. A mass-

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flow meter monitored the carrier flow into the column inlet and a thermocouple measured oven temperature. The outlet mass-flow may decrease by a few percent relative to the inlet mass flow during temperature programming[8], but the possible decrease did not significantly impact these experiments. A microcomputer was used to compare measured flow and temperature data to the flow-rate optimum *vs.* temperature relation. Differences in the comparison were used to adjust flow via a precision flow-control valve driven by a stepper-motor. Improvements in HETP are shown and compared to results from conventional temperature programming.

EXPERIMENTAL

Apparatus

Separations were performed on a Tracor Model 560 gas chromatograph equipped with a flame ionization detector. The silanized column was 183 cm × 2 mm I.D., and packed with 3% OV-17 on 90–100 mesh Supelcoport.

The flow programming system (see Fig. 1) includes a Kurz Model 541 mass-flow meter, a Rockwell AIM 65 microcomputer, a Porter VCD-1000 needle valve flow-controller, a Warner Electric Clutch and Brake Co. SM-024-0018 stepper-motor and digital electronics based upon an ADC-0817 analog-to-digital converter. The GC oven temperature readout (TR) and the mass-flow meter readout (FR) are monitored by the AIM via the analog-to-digital converter. Response time of the Kurz meter was 0.25 sec and measured temperature response time was *ca.* 1 sec.

Based upon an operator-introduced optimum flow *vs.* temperature relation in a BASIC program, the computer causes the stepper-motor to adjust the needle valve. Both the magnitude and sign of the differences between FR and the optimum flow-rate were used to provide pulsing which rotated the stepper-motor, and consequently adjusted the needle valve to compensate for deviations between FR and flow-rate optima. The feedback is monitored during the entire temperature programme. The time constant for the system's response was 3.4 sec. The computer program and detailed electronic circuitry are available from the authors upon request.

Prodecure

Mass-flow *vs.* HETP plots for isothermal elutions were prepared for hydrocarbons at temperatures between 50 and 250°C, with nitrogen as the carrier gas. The 1-μl injections of test solution included: naphthalene (0.23 mg/ml); acenaphthene (0.115 mg/ml); fluorene (0.15 mg/ml); anthracene (0.115 mg/ml); 2-methylanthracene

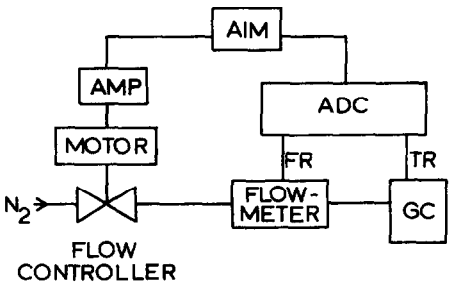

Fig. 1. Block diagram of flow-programming system for temperature-programmed GC separations.

(0.08 mg/ml); fluoranthrene (0.04 mg/ml); pyrene (0.04 mg/ml); chrysene (0.04 mg/ml) 7,12 dibenz[*a*]anthracene (0.02 mg/ml); perylene (0.02 mg/ml); 1,2,3,4-dibenz[*a*]anthracene (0.02 mg/ml). Peak height, area and retention data were evaluated with a Hewlett-Packard 3390A integrator.

Temperature programming was used for hydrocarbon separations using carrier gas flow-rates of 8 ml/min, 23 ml/min, 41 ml/min, and variable flow via flow programming. The oven temperature was raised from 50 to 250°C at a rate of 5°C/min. For conventional temperature-programmed separations without flow programming, flow-rates of 8, 23 and 41 ml/min were set at 50°C, with no further adjustments of the needle valve during the temperature programme.

To generate HETP *vs.* mass-flow data, a constant flow-rate was maintained at the column inlet with isothermal oven temperature. This was achieved by monitoring mass-flow of the carrier gas into the column and adjusting the needle valve. HETP calculations were based on peak widths at half height[9] and the resulting set of flow optima were related to elution temperature (see Fig. 2).

The flow optimum *vs.* elution temperature data were approximated by closed-form functions by least-squares fitting. These relationships were then used in a computer program to calculate optimum flow-rates for each measured TR value during the temperature programme. The calculated optimum flow-rate was compared to FR and the difference between them was corrected via the computer by adjusting the needle valve.

RESULTS AND DISCUSSION

Results from mass-flow *vs.* HETP plots allowed optimum flow-rate values to be determined for the 50–250°C temperature range (see Fig. 2). For oven temperatures below 166°C flow-rate optima, f_{opt}, were characterized by

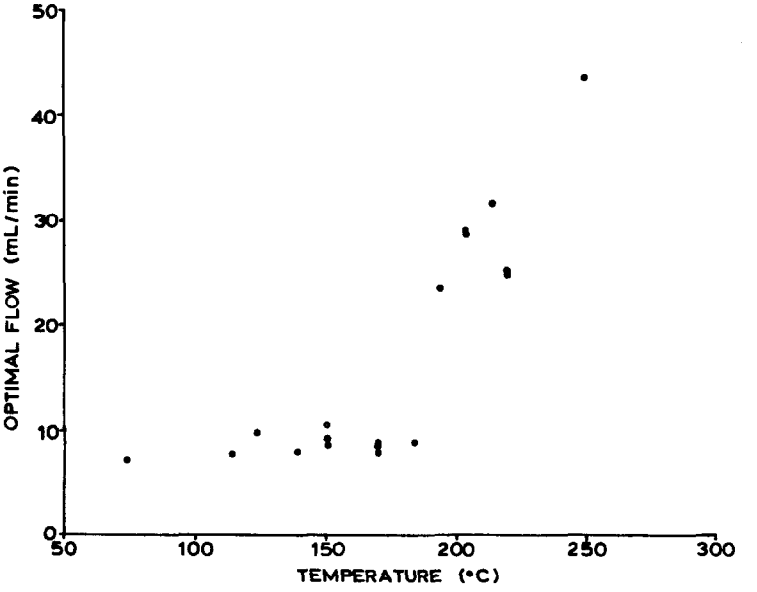

Fig. 2. Optimal flow-rate *vs.* oven temperature, obtained via mass-flow *vs.* isothermal elution data for many temperatures.

$$f_{opt} = 8.58 + 3.672 \cdot 10^{-3} T \quad (1)$$

and for temperatures above 166°C

$$f_{opt} = 4.16 \cdot 10^{2} - 6.594 T + 3.402 \cdot 10^{-2} T^{2} - 5.452 \cdot 10^{-5} T^{3} \quad (2)$$

with f_{opt} in ml/min and T in °C. Eqns. 1 and 2, along with their corresponding ranges were written into a BASIC program for the AIM computer.

Fig. 3 illustrates typical chromatograms achieved with optimized flow programming and temperature programming, and Table I summarizes corresponding HETP data. Table I shows improved HETP values for the flow-programmed system compared to the conventional separations. This was expected because flow *vs.* HETP plots showed relatively sharp minima. Separation power likewise improved as evidenced by several more peaks seen in Fig. 3 for the flow-programmed system as compared to the chromatograms at 23 ml/min and 41 ml/min. At 8 ml/min, later peaks were broad.

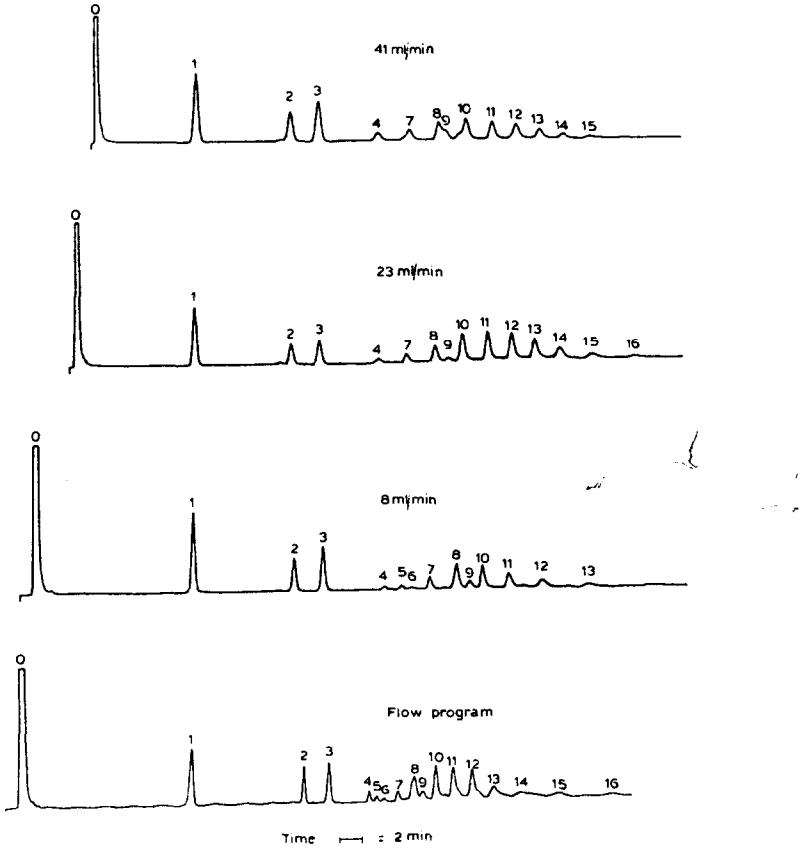

Fig. 3. Chromatograms of a hydrocarbon mixture with temperature programming for various carrier gas conditions: 8, 23, 41 ml/min and optimized flow programming. Peaks: 1 = naphthalene; 2 = acenaphthene; 3 = fluorene; 4–7 = unknown; 8 = 2-methylanthracene; 9 = unknown; 10 = fluoranthrene; 11 = pyrene; 12 = chrysene; 13 = 7,12-dimethylbenz[*a*]anthracene; 14 = perylene; 15 = 1,2,3,4-dibenz-[*a*]anthracene; 16 = unknown.

TABLE I

SUMMARY OF HETP DATA CORRESPONDING TO FIG. 3

Peak No.	*HETP (cm)**			*Flow programming*
	41 ml/min	*23 ml/min*	*8 ml/min*	
1	0.0794	0.0420	0.0179	0.0164
2	0.0300	0.0157	0.00801	0.00325
3	0.0214	0.0124	0.00675	0.00419
4	0.0189	0.0125	0.00463	0.00166
5	NP**	NP	0.00312	0.00166
6	NP	NP	NM***	0.00290
7	0.0166	0.00718	0.00364	0.00337
8	0.0203	0.00639	0.00463	0.00726
9	NM	0.00722	0.00443	0.00368
10	0.0140	0.00568	0.00347	0.00273
11	0.00723	0.00505	0.0465	0.00451
12	0.00650	0.00502	0.00749	0.00515
13	0.00692	0.00562	NM	0.0101
14	0.00283	0.00717	NM	0.0347
15	NM	0.0137	NM	0.0131
16	NP	NM	NM	NM

* HETP $= \frac{L}{5.54}\left(\frac{W_{\frac{1}{2}}}{t_R}\right)^2$, where L = column length (183 cm), $W_{\frac{1}{2}}$ = peak width at half height, and t_R = retention time.

** NP = peak not present or not resolved.

*** NM = not measured.

Microcomputer control along with continuous mass-flow measurements made this flow-feedback system easy to use. Experiments are being done to evaluate effects of mass-flow control upon measurements made both via concentration-dependent detectors and via detectors which respond to the rate-of-delivery of analyte. The use of optimal flow-rates throughout temperature-programmed separations resulted in improved HETP values and separations.

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