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Title: Mass-Flow Control System Utilizing Flow-Feedback

For Gas Chromatography

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A unique mass-flow control system for the carrier gas
in gas chromatography is described and evaluated. Carrier
gas flow is controlled by a flow sensor, feedback elec-
tronics, a flow-control valve and a microcomputer. The
flow-rate is monitored by a mass-flow meter by this system
and the flow is adjusted in response to computer instruc-
tions.

The flow control system was adapted to a new
separations method in gas chromatography; optimized flow
programming with temperature programming. According to
empirically derived flow optima vs. temperature relations,
the microcomputer adjusts the carrier flow-rate according
to a measured-temperature vs. flow-rate format. Improve-
ments in theoretical plate heights are obtained with this
system and results are compared to those achieved via con-
ventional temperature programming.

In another application, a similar system was used to maintain constant mass-flow within 3% (RSD), even during temperature programming. Thus accurate measurements are feasible with detectors which require constant flow throughout their measurement interval, despite temperature changes. Use of the constant-flow system was demonstrated via measurements made by response factor calibration using a Hall Electrolytic Conductivity Detector. Quantitative measurements of impurities in solutions of dieldrin, heptachlor and 1,2,4-trichlorobenzene were achieved without analyte identifications. Similarly, toxaphene was measured without reference compounds identical to each toxaphene eluate.

MASS-FLOW CONTROL SYSTEM UTILIZING

FLOW-FEEDBACK FOR GAS CHROMATOGRAPHY

by

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I. INTRODUCTION

Flow programming in gas chromatography (GC) has several advantages (see below in section on Flow Control Systems for Gas Chromatography). It 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). For example, 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 may be attained (1,3). In flow programmed

systems the inlet column pressure (1,3,5,6) has usually been controlled and the commercially-available DANI system is an example of a pressure-controlled flow programmer (4). A flow control system which uses pressure sensors has been evaluated by Wicar (7). In the work described herein, GC carrier flow-rate is controlled via a flow-feedback system and mass-flow measurements.

HETP vs. Flow vs. Temperature

Column efficiency is measured by the number of theoretical plates, which is the column length divided by the height equivalent of a theoretical plate. Each plate corresponds to a theoretical equilibrium stage that is in series with other stages in a continuous fashion. Normally, the greater the number of plates for a system the better the separation.

The height equivalent of a theoretical plate (HETP), or plate height (H), in gas chromatography is a function of the mobile phase (carrier gas) flow-rate and the temperature of the column or oven. The Van Deemter equation for gas-liquid chromatography with packed columns gives

$$H = 2\lambda d_p + \frac{2\gamma D_g}{u} + \frac{8}{\pi^2} \frac{k'\; d_f^2}{(1+k')^2 D_\ell}\; u \tag{1}$$

where λ is a factor characteristic of the packing, d_p is the particle diameter of the packing, γ is a correction factor for the unevenness of the spaces between the particles, D_g and D_ℓ are the diffusion coefficients of the analyte in the mobile gas phase and liquid stationary phase, respectively, u is the linear gas velocity, k' the capacity factor and d_f is the effective thickness of the liquid film on the support (8,9): k' is a function of the temperature. H can be estimated from a chromatogram of an eluting analyte,

$$H = \frac{L}{5.54} \left(\frac{W_{\frac{1}{2}}}{t_r}\right)^2 \tag{2}$$

where L is the column length, W is the peak width at half height and t_r is the retention time (10).

Van Deemter plots graph HETP <u>vs</u>. carrier gas velocity. Carrier flow-rates are often used instead of velocities for convenience. These plots typically exhibit a minimum corresponding to the velocity or flow-rate giving the lowest HETP value, which corresponds to greatest column efficiency for the specified isothermal conditions (see Section III).

The optimal flow-rate of the carrier gas, which is the carrier flow at the lowest HETP value of a Van Deemter plot, varies with temperature. This is primarily due to changes in k', which is a function of temperature. D_g and

D are also affected by temperature, both increasing with temperature (8). Thus there is a need for carrier gas flow programming for achieving optimal flows during temperature programming.

Necessity of Constant Flow

The sensitivities of concentration-dependent GC detectors are related to the gas flow through the detector (12). Accordingly, as flow of carrier gas changes during a temperature program, so does the sensitivity of the detector. Thus GC methods requiring sensitivity to remain constant throughout an elution may need control of the carrier gas flow. Response factor calibration (RFC) using the Hall Electrolytic Conductivity Detector (HECD) is one quantitative method which requires constant-flow conditions (13).

If the constant sensitivity requirement is met the RFC method may be used to measure chlorinated compounds with a HECD operated in the halogen mode. For RFC, analyte response relative to a response standard must be proportional to the amount of organochlorine eluted (13,14): The HECD is consistent with this requirement (13,14,15). These determinations may be achieved without analyte identifications nor pure reference compounds for each measured eluate.

It should be feasible to maintain constant mass-flow of the carrier gas into the GC column inlet via mass-flow measurements and computer-controlled flow adjustments. However, possible decreases in flow of the carrier gas at the column outlet relative to the inlet during temperature programming (11) may occur. Other temperature effects may also affect measurements. Although temperature programming may be necessary to achieve separations, flow may need to be maintained constant for accurate results. Thus flow through an isothermal detector would be constant, resulting in constant detector sensitivity required by GC methods such as RFC.

Flow Control and Measurement

To control the carrier gas flow, gas chromatographs are equipped with manually controlled valves. These flow control valves are usually orifice-type needle valves such as those manufactured by Porter Instruments. A more elaborate flow controller is manufactured by Brooks Instrument Division of the Emerson Electric Company. The Brooks Model 8744 flow controller utilizes a manually adjusted needle valve along with a pressure sensing diaphragm to maintain a constant pressure differential across the flow controller.

Carrier gas flow can be measured with a rotameter, a bubble meter or a separate flowmeter. GC's usually are equipped with rotameters which are graduated glass tubes containing a free-floating ball. The height to which the ball rises indicates the flow-rate, usually within 10% of the true flow value. Rotameters must be calibrated, as they depend both upon the supply pressure of the gas and upon the gas used.

Bubble meters or separate flowmeters may give more accurate results. An example of a flowmeter is shown in the section entitled The Mass-Flow Meter (see Appendix E) which describes Kurz's mass-flow meter design. A bubble meter is a graduated glass cylinder with an opening at one end for gas to enter. The gas flow-rate is measured via movement of a soap film pushed up the cylinder by the gas; the volumetric movement of the soap film is timed. Usually a bubble meter is used at the column or detector outlet, and results may be very accurate.

Flow Programming Systems

Advantages of flow programming in GC analyses may be summarized as follows:

1. It can shorten analysis times for a wide range of mixtures while allowing the separations at much lower temperatures, for which

the value of the relative retention is usually larger than if flow programming were not used.

2. The number of liquid phases useful for a given separation is increased because one can operate at lower temperatures.

3. Lower operating temperature could be advantageous for thermally unstable samples.

4. The vapor pressure of a liquid increases exponentially with temperature; this is the reason for the exponentially increasing base-line drift during programmed temperature operation. On the other hand, at a given temperature (i.e., at constant partial pressure), column bleeding may increase, at most, linearly with the column flow rate. Thus the background related to the bleeding under isothermal and isorheic conditions is much lower because one is operating at a lower temperature, i.e., only little base-line drift is observed during isothermal analyses.

5. Since the height of the peak is related to the flow-rate, broad peaks can be much more

distinct   under flow programming.   This

may allow for better detection limits (1).

Flow programming and temperature programming have
been combined to reduce anlaysis times and sharpen later
eluting peaks (1,3,4).

Flow control systems for GC (1,3,4,5,6,7) have usual-
ly used pressure measurements and mathematical relations
to monitor carrier gas flow.   Several systems have been
evaluated, but most were designed only for exponential
flow programming (1,3,4,5,6).   Wicar's system (7) also
depends upon pressure measurements but is potentially
versatile as it used microcomputer control and thus should
be easily programmed.

One of the early flow programming systems was des-
cribed as a pneumatically-controlled system (1).   This
system permitted column pressure to rise exponentially
between preset limits during a predetermined time inter-
val.   The controlling component of the system is a pneu-
matic differential-flow valve arranged to permit the
column outlet pressure to be continuously adjusted to
equal the value of the column inlet pressure.   However,
the pneumatic devices permit only limited variations of
flow functions and seldom gave pure exponential forms (5).

Use of a splitter-valve in addition to a gas pressure
regulation   valve   at the column inlet has been demon-

strated by Nygren (5) for use in flow programming. The inlet pressure was regulated with a valve at the carrier gas tank to achieve a suitable range for the splitter valve. After injecting the sample the flow was exponentially raised by manually adjusting the splitter valve. Nygren later developed two other sophisticated flow controllers utilizing mechanical systems controlled by digital electronics (3). One changes flow according to a specified time vs. valve-position relation. This flow programmer used a stepper-motor to control the valve position where one pulse from the digital electronics rotated the stepper motor one step. The other flow programmer adjusted gas flow via a solenoid valve. The frequency of valve openings was controlled and allowed for adjustment of the amount of gas entering the column. Both systems used a cassette tape recorder as the memory unit for storing the flow program signals, which directly controlled the digital electronics. Unfortunately, these devices lacked reliability (4).

Commercially available flow control systems such as the Analabs Flow-Grammer and the DANI flow programmer have been demonstrated (4,6). These systems essentially perform pressure programming at the column inlet. Although these systems seem to be reliable, they lack versatility. The Analabs systems increases the inlet pressure linearly

with time while the DANI relies upon only exponential flow programming.

The use of systems described above assumes that carrier gas flow has a linear relationship to inlet pressure. However, increasing temperature, as in temperature programming, decreases mass-flow due mainly to the increased viscosity and decreased density of the gas. This may cause the flow programming with the above described systems to be inaccurate. Therefore, mass-flow control is an attractive alternative.

Stanislav Wicar has designed a mass-flow controller utilizing microcomputer control (7). This system was designed as an improvement over the Hewlett-Packard electronic flow controller designed for use with the Model 5880A gas chromatograph. The Hewlett-Packard version measured pressure differences but lacked a sensor to monitor explicitly the instantaneous value of the flow-rate. Wicar's system utilized a separate flow-metering device that used semiconductor pressure sensors to monitor inlet pressures of the carrier gas. Using assumed pressure relations, the mass-flow, i.e. the mass of gas passing the measurement device per unit time, of the carrier gas is calculated. The microcomputer was used to control the calculated flow-rates, as well as temperatures of the column oven, injection port, and detector. It also

monitored output from the pressure sensor unit. A demon-
stration of its application has not been published yet.

Mass-Flow Meters for Flow Control

A better approach to flow programming would be to
measure carrier gas flow directly with a mass-flow meter
at the column inlet.   For the research described herein,
Kurz's unique mass-flow meters were used for flow control
systems.   Kurz mass-flow meters measure heat transfer in a
manner which depends on the frequency of molecular colli-
sions with a special transducer, and the measurement thus
compensates for temperature and pressure effects.   These
flow meters measure mass-flow, not volumetric flow rate
(see Appendix E).   Thus supplementary measurements of
pressure and temperature are not required, as for volumet-
ric or differential pressure flow meters. The construction
of these flowmeters makes them rugged, reliable, precise,
and highly accurate for a wide range of conditions (a
photocopy of specifications are included in Appendix E).

The mass-flow of the carrier gas at the column
outlet is equal to the inlet mass-flow with only minor
differences perhaps occurring during temperature program-
ming (11) if the system has no leakage.   Microcomputer
monitoring of mass-flow and subsequent control of flow
could therefore be automated.   The resulting system would

be versatile and effective for flow programming via a variety of flow-programming formats other than simple exponential changes. Also it could be used to maintain constant carrier gas flow to enhance accuracy in quantitative ahalyses.

For a flow programming device to be useful it must be accurate, reliable and versatile. The Kurz flowmeter and microcomputer control ensure these characteristics. Automation with microcomputer control would also make such a system easy to use.

II. THE FLOW CONTROL SYSTEM FOR THIS RESEARCH

A novel flow-control system was developed in this work. This system consisted of a mass-flow meter, an adjustable flow control valve, associated electronics and a microcomputer to control the apparatus. It was used for optimized flow programming with temperature programming (see below, Section III) and constant flow elutions by gas chromatography (see Section IV).

The flow-control system (see Fig. 1) includes a Kurz mass-flow meter (either Model 541 or 1541), difference amplification circuitry (Fig. 3), a Rockwell AIM Model 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 (Fig. 5) based upon a National Semiconductor ADC-0817 analog-to-digital converter. The response time of the Kurz meter was 0.25 sec. and the response time for the measured temperature signal was $\underline{ca}$. 1 sec.

Voltage outputs corresponding to mass-flow (FR) from the mass-flow meter and temperature (TR) from the gas chromatograph, if needed, were monitored by the microcomputer via the analog-to-digital converter (ADC). According to the programming of the microcomputer, the system responds to the presently-measured flow and temperature values by opening or closing the needle valve by way of
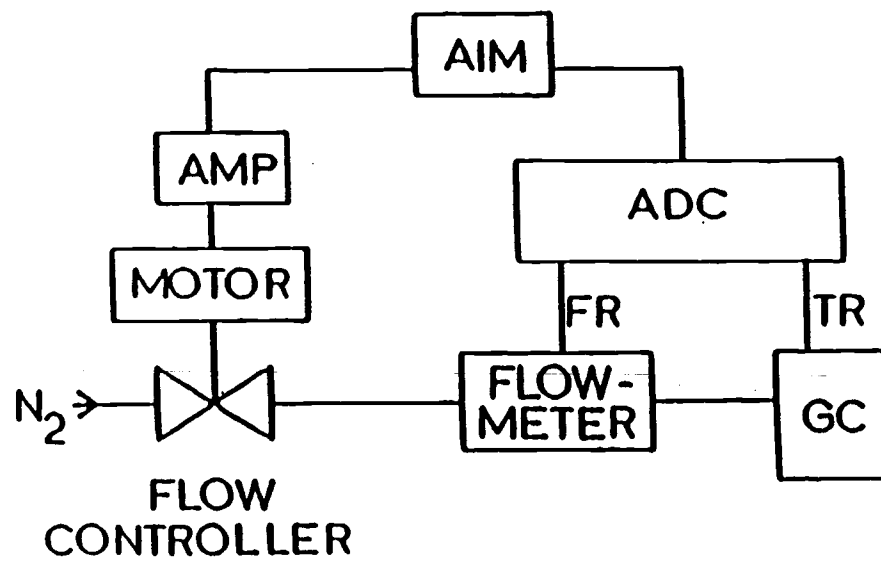
Fig. 1. Flow control system for flow programming with temperature programming

the stepper-motor driven by pulses from logic circuitry (refer to Fig. 6). The adjustment causes changes in carrier gas flow, if desired, by the system. After each stepper-motor increment TR and FR are again read by the computer and the next comparison made. The flowmeter and the gas chromatograph temperature outputs are compared at a frequency of 4 Hz. This reiterative logic is continued for flow-feedback control throughout a chromatogram.

The gas chromatograph used was a Tracor Model 560 with a flame ionization detector (FID) and a Hall Electrolytic Conductivity Detector (HECD). The detector outputs were monitored by a Hewlett-Packard 3390A integrator to obtain peak areas and half-widths. All experiments were done on a silanized packed column, 183 cm long, 2 mm I.D., and packed with 3% OV-17 on 80/100 mesh Supelcoport.

<u>Mass-Flow Meter</u>

As shown in Figure 2, the mass-flow probe, or sensor, is in the flow path of the carrier gas. Swagelock male connector tube fittings were used on both ends of the flowmeter. These fittings were 1/8" O.D. tube fitting to 1/16" male pipe threads. All gas lines were 1/8" O.D. copper tubing.

The flow sensor is heated and operated as a constant-temperature thermal anemometer. It responds to the mass-
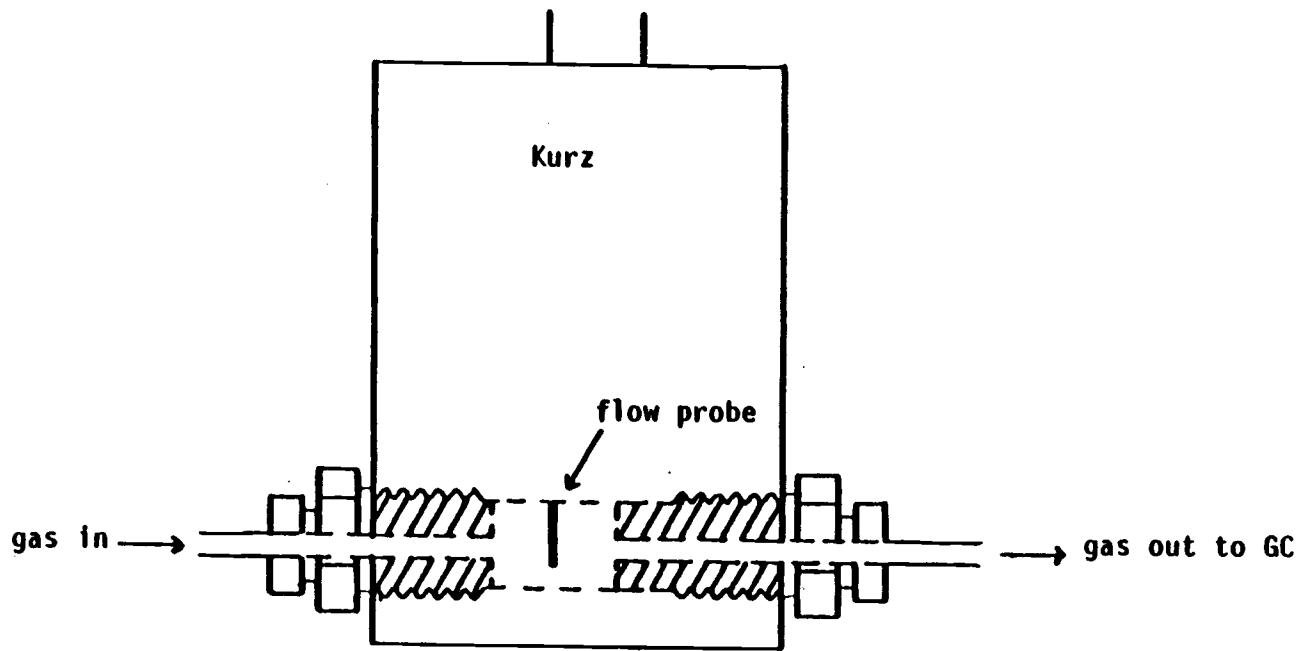
Fig. 2. Mass-flow probe of the Kurz flowmeters

flow by sensing the cooling effect of the gas as it passes over the heated flow sensor (see Appendix E). This cooling of the sensor is due to heat transfer from the sensor caused by gas molecules or atoms colliding with the sensor. The flowmeter is actually measuring the product of density and velocity of the gas (16). A temperature sensor is incorporated into the design and allows compensation for ambient temperature variations over a range of $-55^{\circ}C$ to $125^{\circ}C$ (manufacturer specifications). Thus the measurement is compensated for pressure and temperature, i.e. density changes. The output corresponds to mass-flow in units of standard liters per minute ($25^{\circ}C$, 1 atmosphere). Gas type or composition affect the response of the flowmeter, as different gases have different heat transfer characteristics. Both Models 541 and 1541 were calibrated with air by Kurz Instruments.

Difference Amplifier

The outputs from the flow meters were amplified (Fig. 3) so that the voltages would be in the range of 0 to 5 volts for N_2 gas flows of 0-60 mL/min. Components of the circuit in Figure 3 included an Analog Devices AD-522B instrumentation amplifier and a Texas Instrument TL-081 operational amplifier. Difference amplification was used for the Kurz Model 541 output taken from pin 9 of the
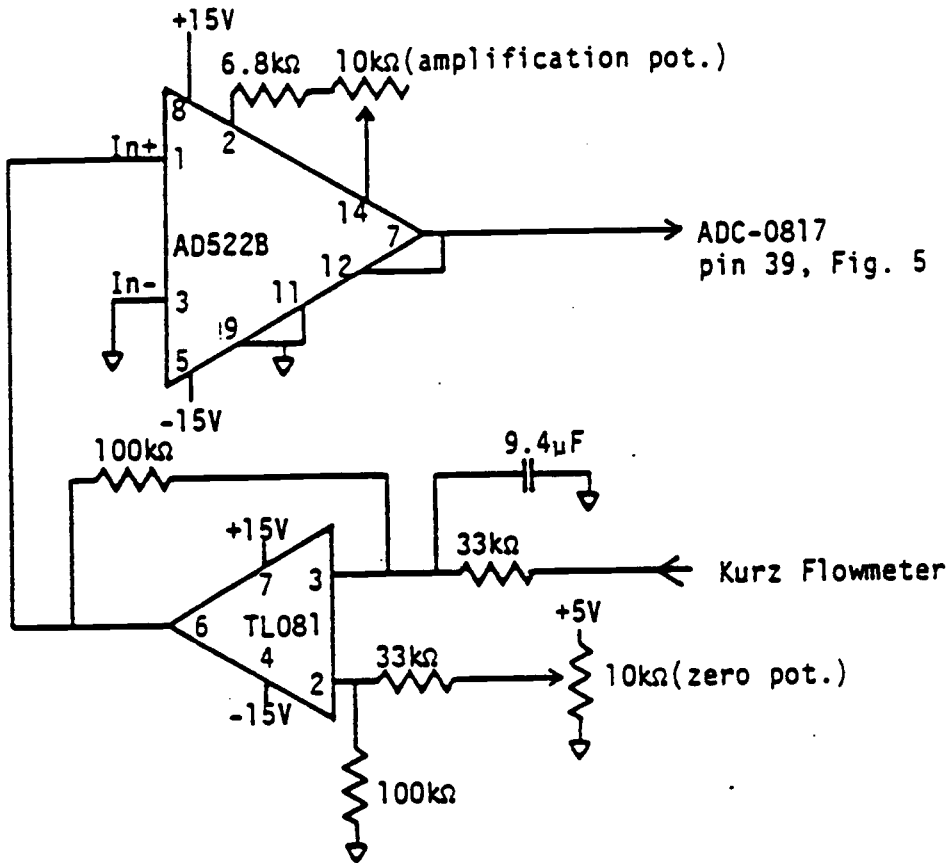
Fig. 3. Difference amplifier

LM-324N operational amplifier chip in the circuitry of the flow meter. Its common was grounded with the amplifying circuit. The voltage signal at pin 9 was about 1.6 volts at 0 gas flow and increased with flow. The 1.6 volts was nulled by adjusting the zero-adjustment potentiometer at no flow (refer to Fig. 3). The voltage corresponding to flow after adjusting for zero flow was amplified and set by the amplification potentiometer. Amplification was adjusted so 60 mL/min. of gas flow corresponded to 4.75 volts at pin 7 of the AD-522B after difference amplification. The circuit was powered by a Polytron Devices Inc. triple power supply Model P51-15 (+15, -15 and +5 volts DC, .250 amp). This and all other circuits were placed on a Radio Shack Hobby Board no. 276-154A.

This circuit is described as a difference amplifier because it compares two voltages and amplifies the difference. The flowmeter's voltage output is attached to pin 3 of the TL-081 by way of a low pass filter. The zero offsetting potentiometer is part of a voltage divider circuit and provides a variable voltage to pin 2 of the TL-081. The TL-081 circuit compares the voltages and amplifies the difference by a factor of 100/33 as dictated by the resistors (100k Ω and 33kΩ) used. The amplified output from the TL-081 (pin 6) is connected to pin 1 of the AD522B instrumentation amplifier. Using the AD522B

allows for versatility in amplification of the pin 1 voltage as the resistance between pins 2 and 14 (R_A) may be varied with the amplification potentiometer. Thus, the voltage from pin 6 of the TL-081 will be amplified by a factor of $1 + 2\times10^5/R_A$ by the AD522B.

Zero-adjustments at zero gas flow did not have to give exactly 0 volts because the microcomputer was programmed to treat the initial flow reading, with the flow-control valve closed, at the start of the program as the voltage at zero flow. This zero flow value was subsequently subtracted from measured flow values to obtain the true flow value. However, only positive voltages may be measured by the ADC-0817 as this ADC is unable to properly respond to negative voltages.

The voltage output from the Kurz Model 541 had an AC component (60 Hz) which was evident in the output of its LM-324N operational amplifier. This noise caused negative voltages to be delivered to the ADC-0817. To prevent this, a low-pass filter was used on the output of the LM-324N (see Fig. 3) and this introduced a time constant of 0.31 seconds.

A nearly linear response was found for the Kurz 541 after difference amplification in the flow range of 0 to 60 mL/min. This flow range corresponds to a voltage range from the amplification circuit of 0 to 4.75 V, which cor-

responds to an analog-to-digital conversion of 0 to 243 by the ADC-0817 (Fig. 4). Linear least squares fitting of various flow values to the resulting binary output gave a best fit function of

$$Y = -.9296 + 3.436 \ X + 1.605 \times 10^{-2} \ X^2 \qquad (1)$$

where X is the gas flow in mL/min and Y is the gas flow in binary code as would be read by the AIM 65 (see Fig. 4).

The output from the Kurz Model 1541, used with helium, had a linearizing circuit which allowed reading of a DC output which changes linearly with gas mass-flow. When using the Model 1541 flowmeter the amplification potentiometer was readjusted to give 4.75 volts at pin 7 of the AD-522B for a flow of 52 mL/min. The zero potentiometer along with the amplification potentiometer were used to yield 0.29 volts for 3.16 mL/min or one full revolution of the flow valve. Achieving 0 volts for no helium gas flow was too difficult since helium has a high diffusion rate. The Model·1541 gives a non-zero output even with no helium flow due to helium's high heat transfer characteristics, thus the output of the flowmeter may change as helium dissipates. The negative output of the flowmeter was grounded.

Unlike the Model 541, the 1541 was able to respond to changes in gas flow of helium. Helium with its greater
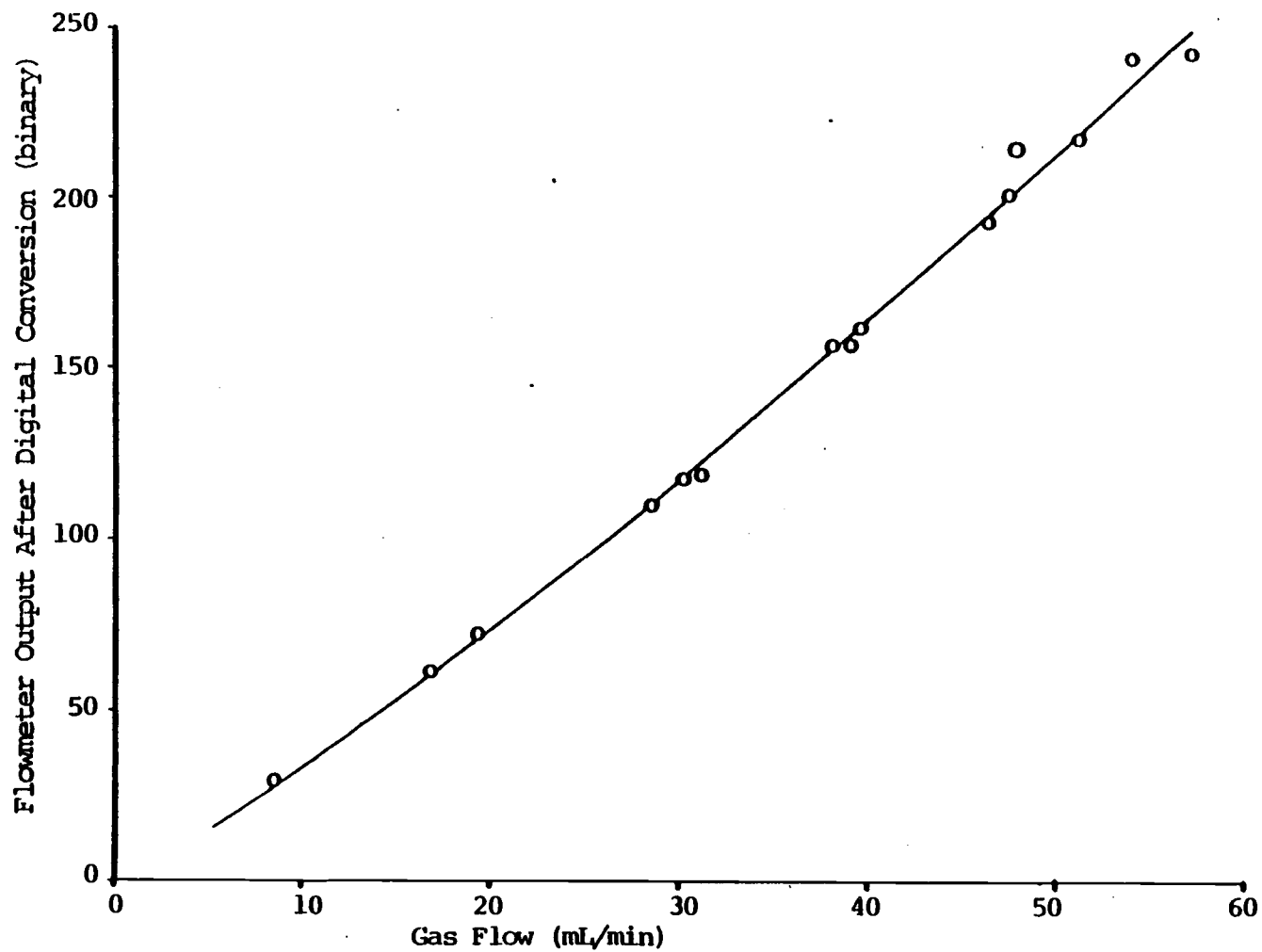
Fig. 4. Gas flow vs. flowmeter output after digital conversion

heat transfer characteristics due to its low density, causes the 541 to reach near-maximum response with no He flow. The 1541 is designed for a greater range of mass-flow values and thus is able to respond to small changes in He flow.

Microcomputer Interfacing

Components used for interfacing the GC oven tempe-rature output and flowmeter output to the AIM micro-computer included the National Semiconductor ADC-0817, a Signetics LM-555 timer, a Texas Instruments TL-081 opera-tional amplifier and a Rockwell AIM breakout panel (Fig. 5).

The difference amplifier output corresponding to mass-flow of carrier gas was sampled by the ADC-0817 and the digitized signal was read by the AIM 65 microcomputer. The ADC-0817 has 8-bit resolution, a 0-5 volt range of conversion and may sample analog signals from 16 sources.

The ADC-0817 can convert analog signals from 16 dif-ferent sources since it has a 16-channel multiplexer. To control which channel is being converted, a 4-bit address control is used. The oven temperature voltage from test point one (TP1) of the Tracor 560 circuitry was attached to channel 0, pin 38, through a voltage-follower circuit, using a TL-081 operational amplifier. The flowmeter
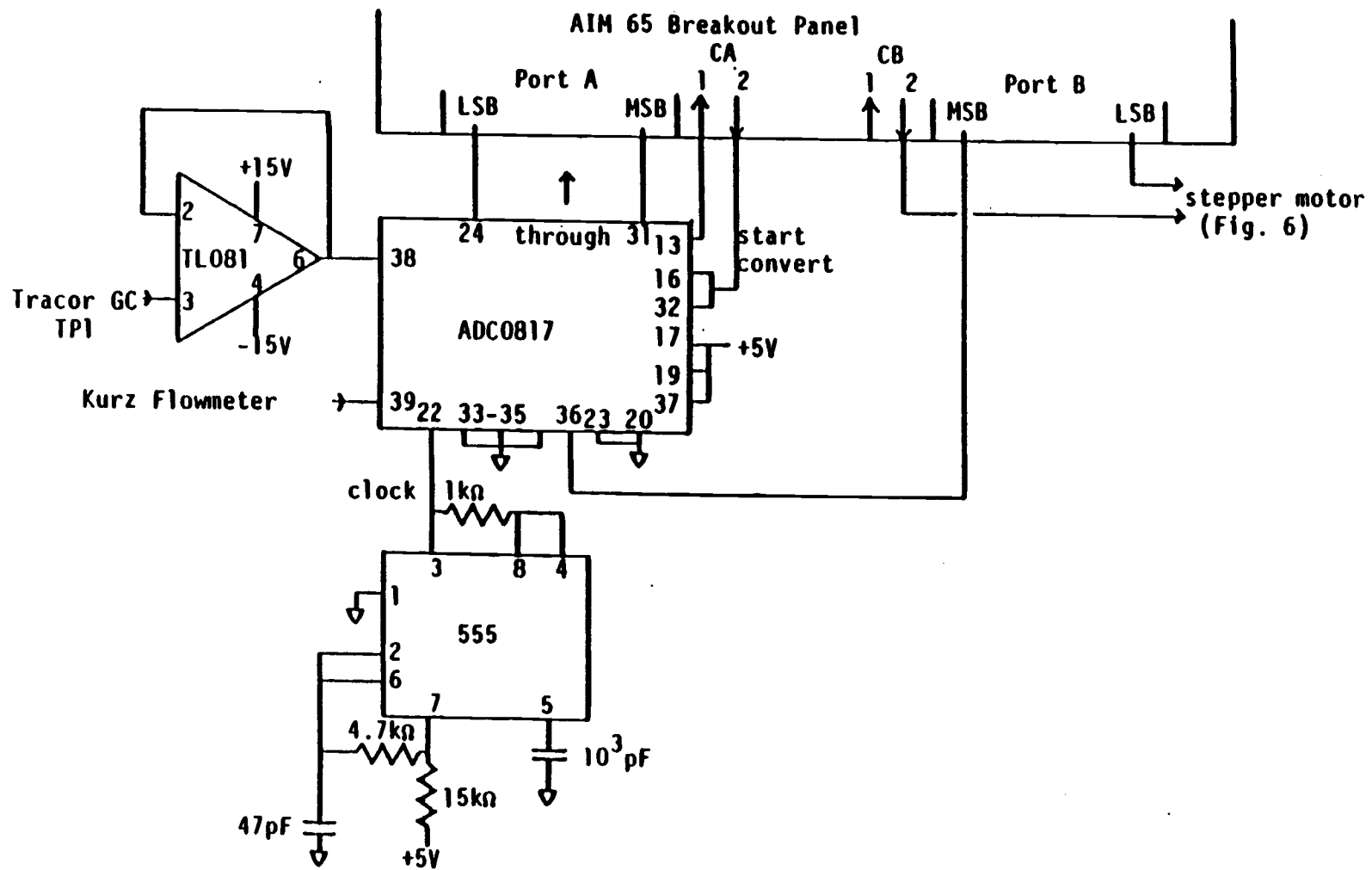
Fig. 5. Microcomputer interfacing

voltages, after difference amplification, were attached at channel 1 (pin 39, Fig. 5). The voltage follower keeps the circuit from drawing too much current from the Tracor 560,

Testpoint 1, TP1, on the Programmer Analog and Heater board number 11466-0001 of the Tracor Model 560 gas chromatograph, is connected to the output of an operational amplifier (part number U19741) in the gas chromatograph's electronic circuitry. This operational amplifier follows the response of the thermocouple (TC) to the oven temperature and amplifies that response yielding a voltage at TP1 of 1 volt per $50^{o}C$ rise with a 0 volt output corresponding to $0^{o}C$. The voltage follower protects operational amplifier U19741 by limiting the current drawn; high currents might damage it.

When address-bit A (pin 36) on the ADC-0817 is low, i.e. grounded, the AIM microcomputer is able to read the ADC output for the oven temperature voltage by monitoring the 8-bit output port of the ADC-0817, pins 24-31. This is done with the computer program by having 0 sent to its most-significant-bit (MSB) of Port B (see below). The output port of the ADC-0817 was connected to Port A on the peripheral attachment of the AIM micrcomputer. Port B of the microcomputer was used as an output port to interact with the ADC-0817 and to access logic circuitry of the

stepper motor (detailed below). Holding address bit A high, i.e. +5 volts, or 1, sent to MSB at Port B by the program, caused A/D conversion of the flowmeter output voltage. Bits B, C, and D (pins 33 to 35) of the address control were grounded since only 2 channels were needed. Figure 5 shows connections of the microcomputer peripheral devices to the ADC-0817 and stepper-motor logic circuitry.

Conversion of analog voltage signals to digital signals compatible with the AIM microcomputer at pins 24-31, Port A, is actuated by a +5 volt pulse at pin 16 of the ADC-0817 from CA2 of the microcomputer (Fig. 5). The pulse to the "start convert" pin 16 begins an electronic cycle which converts the voltage at either pin 38 or pin 39 to a digital form. Pin 38 is connected to TP1 of the Tracor GC and pin 39 is connected to the output of the difference amplifier for flow measurement. Pin 36 of the ADC-0817 controls which conversion occurs: +5 volts at pin 36 causes voltage at pin 38 to be converted, 0 volts allows for conversion of the voltage at pin 39.

The duration used for conversion depends on the circuit and the 555 timer, shown in Fig. 6. It produces a pulse, or cycle, frequency of 1.26 MHz which is connected to the timing counter or "clock" at pin 22 of the ADC-0817. Thus for a 0 to +5 volt range of conversion, which

complete 256 cycles. Each cycle can be considered as an increment of 5/256 volts beginning at 0 volts and ending at 5 volts. When enough cycles have been completed such that the incremented voltage equals the voltage at either pin 38 or 39, the number of completed cycles is counted by the ADC-0817 and this number is provided to pins 24-31 of the ADC with pin 31 being the 2^0 position and pin 24 corresponding to 2^8. These voltages at Port A are translated as a binary number by the microcomputer.

The BASIC program used by the microcomputer acts upon the voltage sequence at pins 24-31 when a +5 volt signal is provided at CA1 by pin 13 of the ADC. After pins 24-31 have been read by the microcomputer a +5 volt pulse is again provided by CA2 to pin 16, initiating another ADC conversion.

Microcomputer Programming

The main programs for flow-control with the AIM microcomputer were written in Microsoft BASIC, and a machine-language subroutine was used to open the needle valve by controlling the logic circuitry of the stepper motor, and another subroutine closed the needle valve when called by the BASIC program. Another special subroutine was used for reading the flowmeter output via the Analog Devices AD-522B and the oven temperature voltage via the

voltage follower.   Other subroutines were used to prepare
the peripheral control register for proper sending and
receiving of logic signals.   These programs are shown in
Appendices A, B, and C.

For both projects, optimized flow programming with
temperature programming and maintaining of constant car-
rier gas flow with temperature programming, the same
subroutines were used (See Appendix A).   However, dif-
ferent BASIC programs were used, as shown in Appendices B
and C.   The reading of the gas flow and oven temperature
were done repeatedly by the main programs throughout the
chromatography by calling for the subroutines.   However,
for constant-flow experiments, oven temperature data were
not needed.

Machine Language Subroutines

The first machine language subroutine, Assignment of
Peripherals, listed in Appendix A is essential to both
BASIC programs.   The first two commands set Port B (cell
location A000) as an output port, meaning its bits will be
used to transmit high or low signals, and the next two
commands set Port A (cell location A001) as an input port
as all its bits will be used to receive the output of the
ADC-0817.   Lines 7 and 8 load the binary hexadecimal value
E9 into cell location A00C which is the peripheral control

register. This allows the actions of CA1 and CA2 as described above. Lines 9 and 10 load the value 0 into Port B. Then with all the bits low including the MSB (most significant bit, 2^8), conversion will take place for the GC temperature output. Line 11 will read Port A, thus causing a pulse to be sent by CA2 to begin ADC conversion. When the conversion is complete, signaled by +5 volts at CA1, the interrupt flag register (cell A00D) is checked for +5 volts at bit 1 (decimal value 2), in cell A00D via the commands on lines 12, 13, and 14. When this occurs Port A is read and its value is stored at cell location 0E00 which the BASIC program will find as decimal value 3584.

A machine-language subroutine program, Reading the Flow, has the MSB of Port B high which will initiate conversion of the flowmeter input at pin 39 of the ADC-0817 according to the commands of the first two lines of this program. Again the interrupt flag register is checked for completion of conversion in lines 5, 6 and 7. The value at Port A is read and stored at cell location 0E01 as shown in lines 8 and 9. 0E01 has a decimal value of 3585 as this value is used by the microcomputer to read the flow at cell location 0E01.

The subroutines, Stepping the Motor in the Open Direction and Stepping the Motor in the Close Direction,

both have hexadecimal value A9 in the peripheral control register as shown by lines 1 and 2 of both programs. A9 in the peripheral control register will allow a +5 volt to 0 volt pulse of a duration of 1 microsecond to be sent out via CB2 to the stepper motor logic circuitry (see Fig. 5 and 6) whenever a value is stored at Port B. The stepper motor responds to this pulse by incrementing its rotational position and, depending on whether the least significant bit (LSB 2^0) of Port B is held low (0V) or high (+5V), this step will be in either the open or close direction for the flow control valve, respectively. Lines 3 and 4 of the Stepping the Motor in the Open Direction program sets the LSB to 0V, while the same lines in the Close Direction program sets the LSB to +5V.

Computer Program for Optimized Flow

The BASIC program for Optimized Flow Programming with Temperature Programming (Appendix B) uses the machine language subroutines described above by calling for their use with POKE statements. Line 10 calls for the machine language subroutine Assignment of Peripherals and line 12 initiates execution of the subroutine. The RTS statement in each subroutine (Appendix A) causes the computer to return to the next line in the BASIC program. To obtain the temperature or flow results after conversion, PEEK

statements are used to assign the converted values to variables (X and F) in the BASIC program. Lines 30 and 40 calculate an optimal flow value (Y) as a function of each oven temperature value (X), while lines 100 through 120 compare the digital representation of the measured flow value (F) to Y. If F and Y are not equal, then one of the subroutines, Stepping the Motor in the Open Direction or Close Direction, are called by the BASIC program via lines 130 and 170. The program then returns to line 10 to reset the peripheral control register and again reads digital representation of the temperature signal, thus reiterating the program continuously throughout a chromatogram. To stop the program, the key F1 on the keyboard of the AIM microcomputer is pushed.

Computer Program for Constant Flow

The Constant Flow Program (Appendix C) is initiated by the user-assigned flow value (F) through a keyboard sequence. This is automatically followed by setting of the peripheral control register (lines 20 to 25). Although the subroutine Assignment of Peripherals, described above, reads the digital representation of the temperature signal, this BASIC program does not use it. Signal averaging is used for the initial flow value after the needle valve has been opened one full revolution (lines 40

through 130); this corresponds to a He flow of 3.16 mL/min at 40 p.s.i. (refer to the section The Mass Flowmeter).

Using the average zero flow value (A) for a gas flow of 3.16 mL/min, the equation relating digital representations of flow values and measured flows, mL/min, is established (line 140). The slope for this relation is calculated by assuming a linear relation between the digital output of the Kurz 1541 and mass-flow (0 to 243 in digital format corresponding to 0 to 52 mL/min flow). Calculating a new intercept value for the linear relation each time this program is iterated precludes the need to set a digital zero-flow value for 0 mL/min via the difference amplifier. Lines 150 to 250 read the digital representation of the measured flow value. After signal averaging (line 240) this averaged flow value (X) is converted to mL/min using the calculated relation. The digital representation of the average measured flow (X) is compared to the user-entered flow value (F). If they are not equal the subroutines for stepping the motor are initiated (lines 260 to 340), as described above. This program is reiterated continuously, returning back to line 150, until stopped by depressing F1 on the microcomputer keyboard.

Control of the Stepper-Motor

The AIM microcomputer is able to adjust the flow con-
troller needle valve by way of the stepper motor (see
above). Logic circuitry (refer to Fig. 6) consisting of a
National Semiconductor binary hexadecimal counter
(DM74191N) and 3 National Semiconductor exclusive-or-gates
(DM-7486N) were manipulated by the microcomputer to send
voltages to the bases of 4 National Semiconductor power
transistors (TIP112, 1.0 amp) in a specified sequence.
The transistors were kept properly cooled with heat sinks
and 1.0 amp diodes (IN4005) were used to protect against
reverse flow of current through the transistors. Two
transistors at a time have 0.87 amp of current through
each when these two transistors have a voltage applied at
their bases. This current flows through two of the four
stepper motor coils creating a magnetic field to rotate a
permanent magnet on the shaft of the motor. The 74191 and
7486 were powered by the Polytron P51-15 and the coils of
the stepper motor were connected (black lead) to a Power
One HB5-3/OVP-A (5 volts, 3 amps) power supply.

4:1 reduction of rotation was achieved by a gear on
the stepper motor shaft and a gear of 4 times larger
diameter attached to the needle valve (see Fig. 7): rota-
tion of the valve is achieved with a non-slip belt.
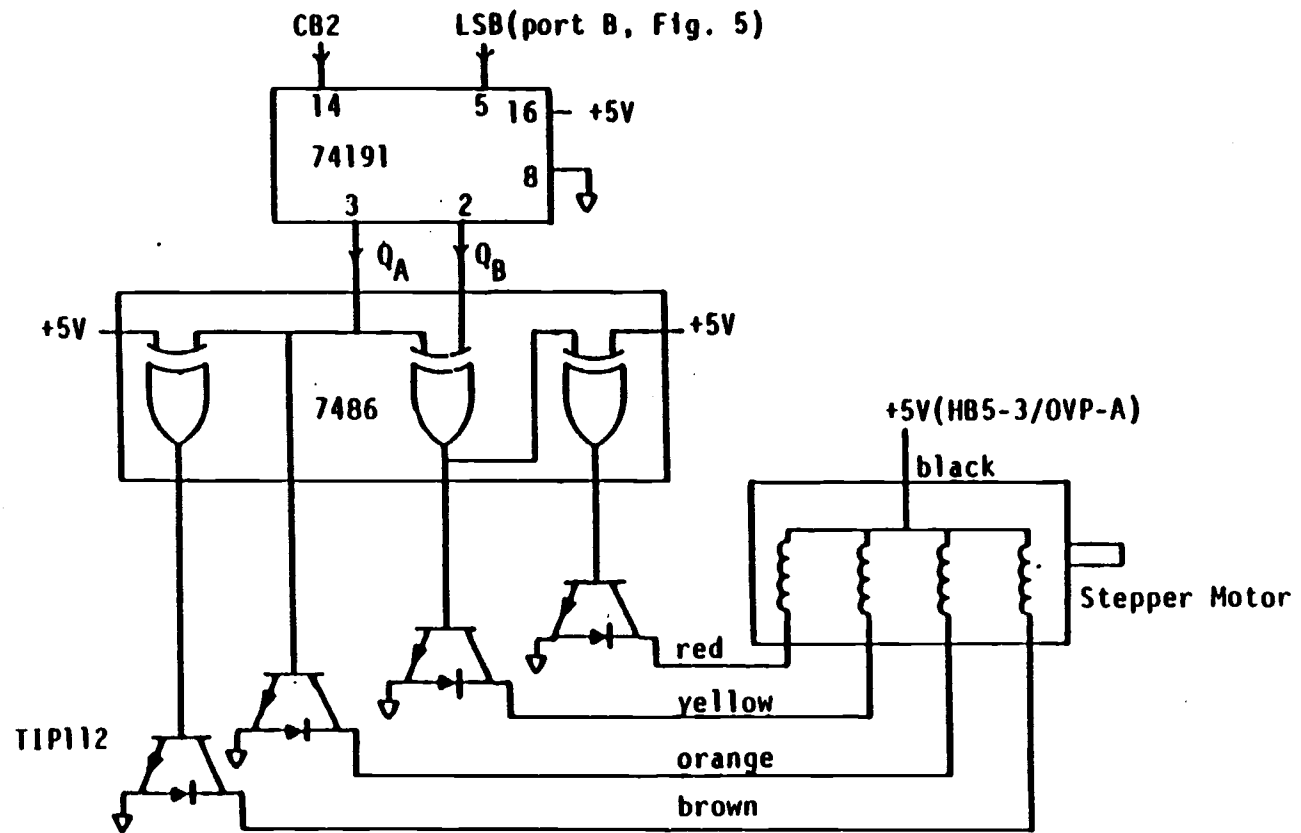Stepping the motor to control the needle valve is done by
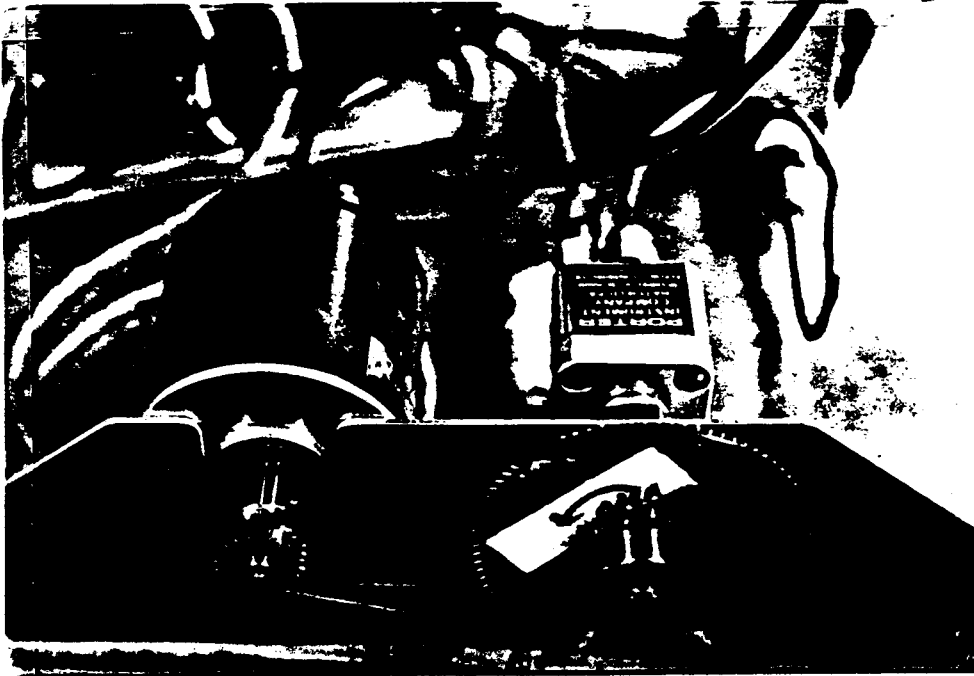
Fig. 6. Stepper motor logic circuitry

Fig. 7. Configuration for the stepper motor (left) and the
flow controller needle valve

having the 74191 counter count either backwards or forwards. Each iteration of a subroutine designed to drive the stepper motor steps the motor only one movement increment.

III. <u>OPTIMIZED FLOW PROGRAMMING WITH TEMPERATURE</u>
<u>PROGRAMMING FOR GAS CHROMATOGRAPHY</u>

Optimized flow programming was achieved in this work.
HETP <u>vs.</u> flow plots at different temperatures yielded
their respective flow-rate optima. These optima were used
to establish optimum flow <u>vs.</u> temperature relations.
These relationships were then used to select and regulate
carrier flow during temperature programmed separation.   A
mass-flow meter monitored the carrier flow into the column
inlet and a thermocouple measured oven temperature: the
outlet may decrease by as much as a few percent relative
to the inlet mass-flow during temperature programming
(11), but the possible decrease did not significantly
impact these experiments.   A microcomputer was adopted to
compare measured flow and temperature data with the flow-
rate optimum <u>vs.</u> temperature relation. Differences in the
comparison were used to adjust the flow via a precision
flow-control valve driven by a stepper motor.   Improve-
ments in HETP are shown and compared to results for con-
ventional temperature programming.

<u>Apparatus</u>

Separations were performed on the Tracor Model 560
gas   chromatograph equipped with a flame ionization

detector. The silanized column was 183 cm long, 2 mm I.D., and packed with 3% OV-17 on 80/100 mesh Supelcoport.

The flow programming system (see Fig. 2) 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 a National Semiconductor analog-to-digital convertor ADC-0817. The GC oven temperature readout (TR) and the mass-flow meter readout (FR) are monitored by the microcomputer via the analog-to-digital convertor. 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 program. The computer program and detailed electronic circuitry are shown above and in the Appendices.

Procedure

Mass-flow vs. HETP plots for isothermal elutions were prepared for hydrocarbons at temperatures between 50°C and 250°C, with N_2 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 (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); per-ylene (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 programming. The oven temperature was raised from 50°C 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 program.

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 temperatures (see Fig. 9).

The flow optimum vs. elution temperature relation was 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 program. The calculated flow-rate was compared to FR and the difference between them was corrected via the computer and stepper motor by adjusting the needle valve.

Results and Discussion

Results from mass-flow vs. HETP plots allowed optimum flow-rate values to be determined over the $50^\circ C$ to $250^\circ C$ temperature range (see Fig. 9). An example of a plot achieved in this work is shown in Figure 8. For oven temperatures below $166^\circ C$ flow-rate optima, f_{opt}, were characterized by

$$f_{opt} = 8.58 + (3.672 \times 10^{-3})(T), \text{ and} \qquad (2)$$

for temperatures above $166^\circ C$

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

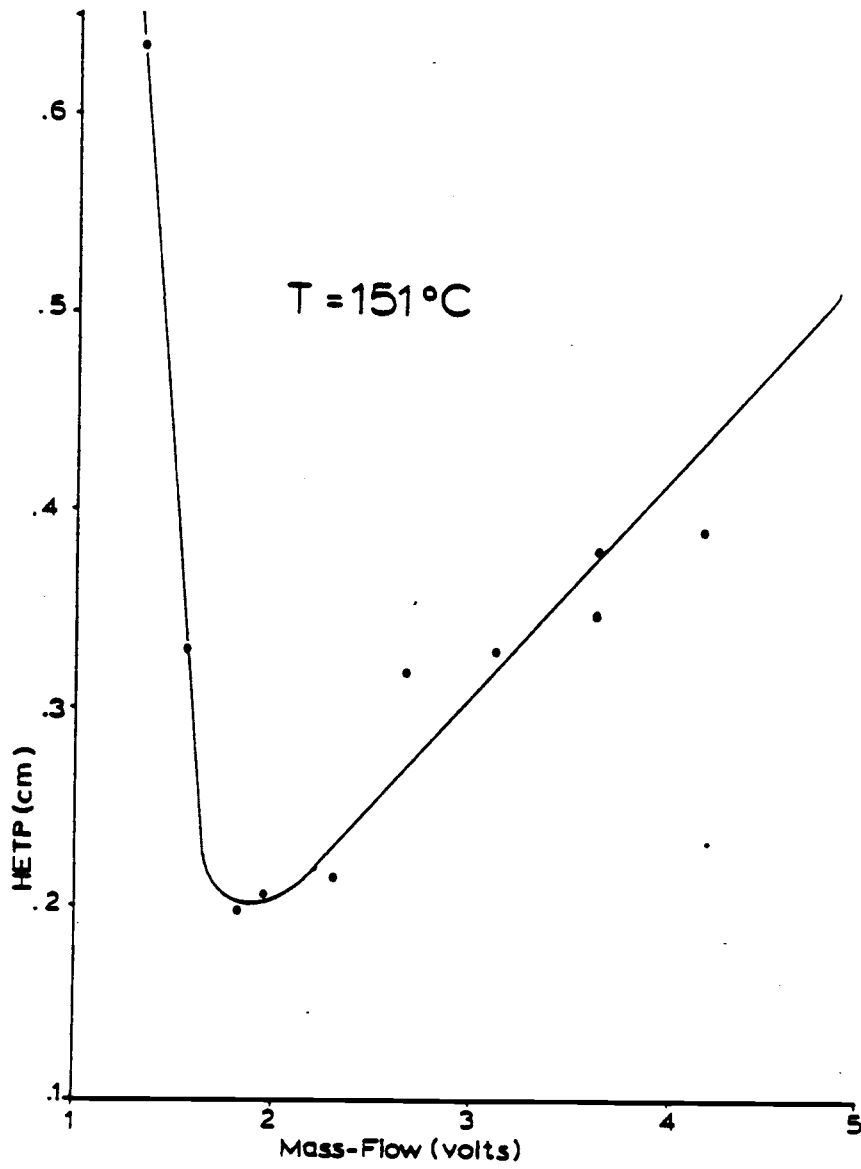with f_{opt} in mL/min and T in $^\circ C$. Equations 1 and 2, along

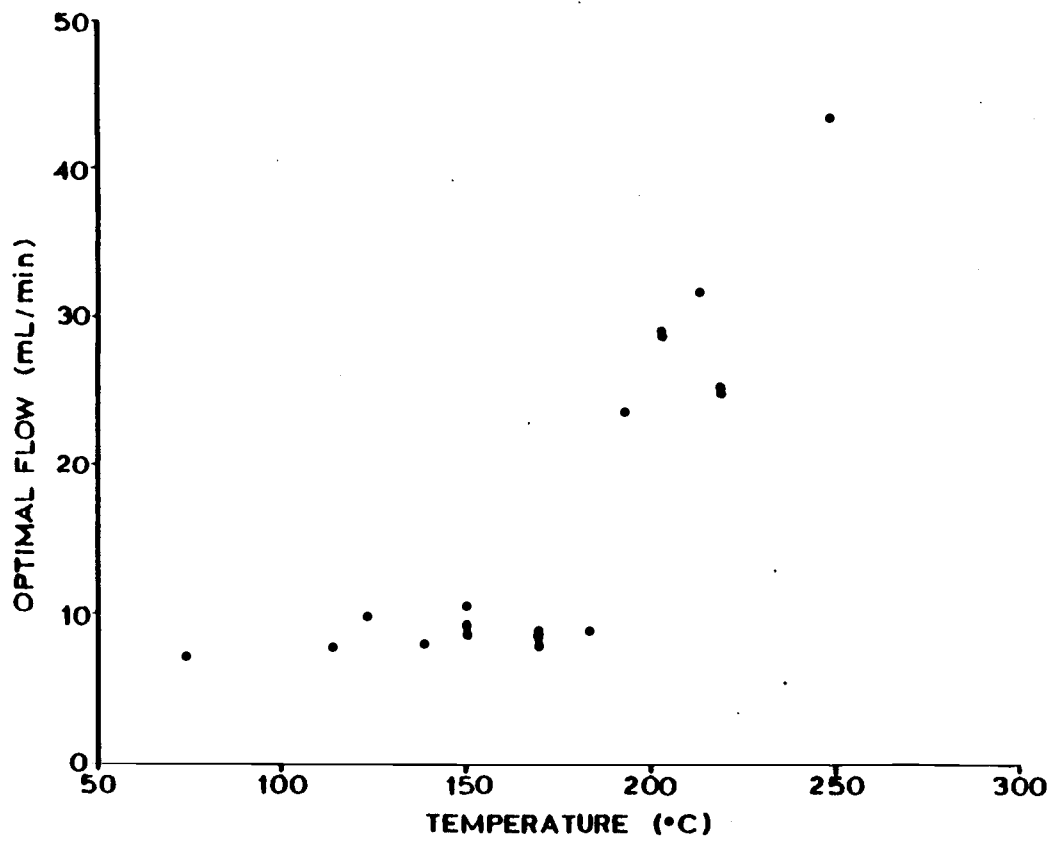Fig. 8. Carrier gas flow vs. HETP at 151°C

Fig. 9. Flow optima vs. temperature

with their corresponding ranges were written into a BASIC program for the AIM computer.

Figure 10 illustrates typical chromatograms achieved with optimized flow programming and temperature programming, and Table 1 summarizes corresponding HETP data. Table 1 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 Figure 10 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.

Microcomputer control along with continuous mass-flow measurements made this flow-feedback system easy to use. The use of optimal flow-rates throughout temperature programmed separations resulted in improved HETP values and separations.
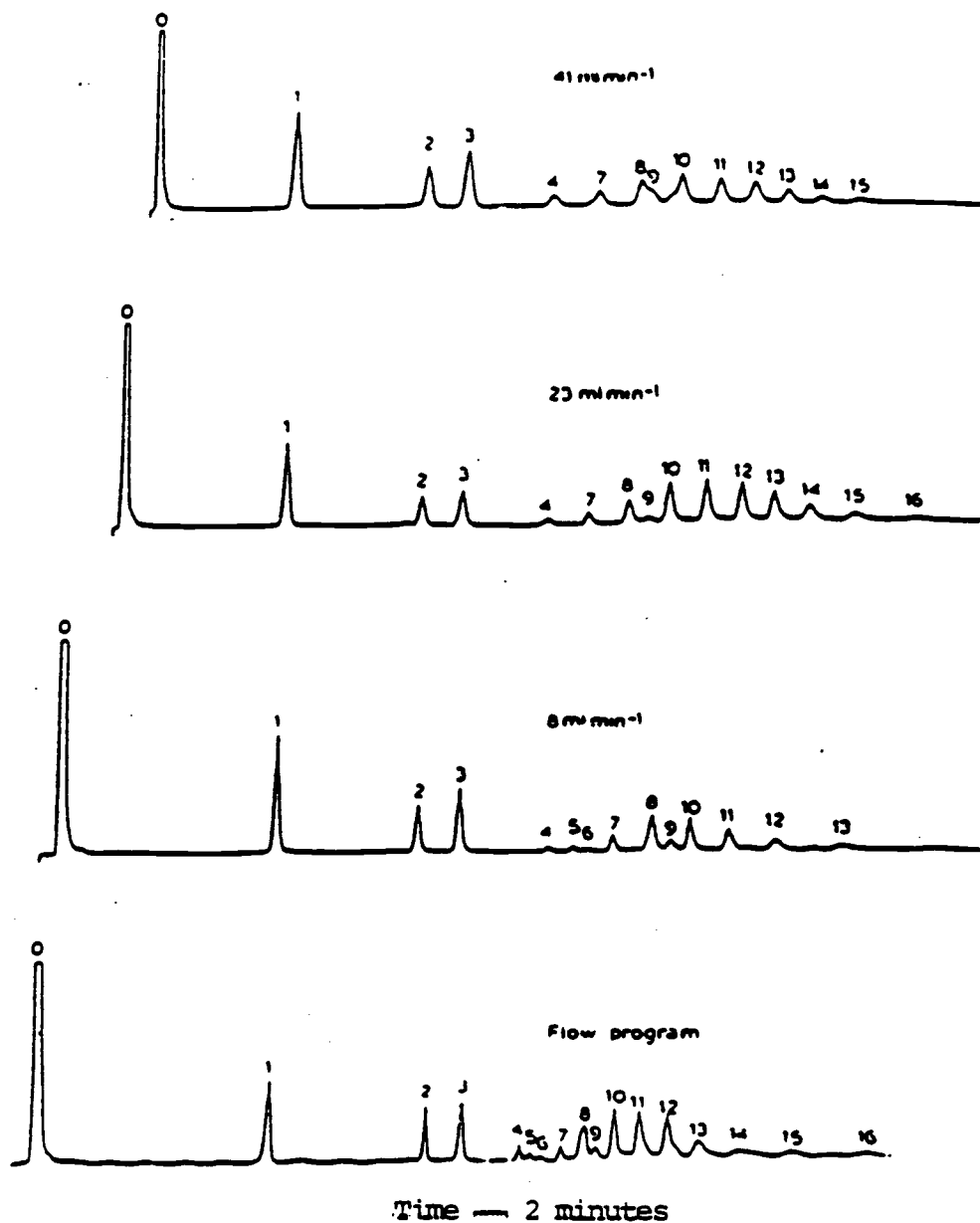
Fig. 10. Chromatograms of a hydrocarbon mixture with temperature programming for various carrier gas conditions. Peaks: 1=naphthalene; 2=acenaphthene; 3=fluorene; 4=unknown; 5=unknown; 6=unknown; 7=unknown; 8=2-methylanthracene 9=unknown; 10=fluoranthrene; 11=pyrene; 12=chrysene; 13= 7,12-dimethylbenz(a)anthracene; 14=perylene; 15=1,2,3,4-dibenz(a)anthracene; 16=unknown.

Table 1

*HETP (cm)

Peak #	41 mL/min	23 mL/min	8 mL/min	Flow Pro-gramming
1	.0794	.0420	.0179	.0164
2	.0300	.0157	.00801	.00325
3	.0214	.0124	.00675	.00419
4	.0189	.0125	.00463	.00166
5	MP	MP	MM	.00166
6	MP	MP	MM	.00290
7	.0166	.00718	.00364	.00337
8	.0203	.00639	.00463	.00726
9	MM	.00722	.00443	.00368
10	.0140	.00568	.00347	.00273
11	.00723	.00505	.0465	.00451
12	.00650	.00502	.00749	.00515
13	.00692	.00562	MM	.0101
14	.00283	.00717	MM	.0347
15	MM	.0137	MM	.0131
16	MP	MM	MM	MM

$$*HETP = \frac{L}{5.54} \left(\frac{W_{\frac{1}{2}}}{t_r}\right)^2$$

L - column length (183 cm)

$W_{\frac{1}{2}}$ - peak width at half height

MP - peak not present or not resolved

MM - not measured

IV. CONSTANT MASS-FLOW FOR GAS CHROMATOGRAPHY

Quantitative measurements were made using RFC (see Appendix F) with a HECD for toxaphene and for impurities in solutions of dieldrin, heptachlor and 1,2,4-trichlorobenzene. These determinations were achieved without analyte identifications, nor did they require pure reference compounds for each measured eluate. Temperature programming was used for the analyses with constant flow of the carrier gas maintained via the flow control system.

Reagents

Reference substances were purchased from Aldrich Chemical Company: 1-chlorooctane (1COA, 99% pure), 1,2,3-trichloropropane (TCPrA, 99+% pure), (1,5-dichloropentane (DCPeA, 99% pure), 1-chlorobenzene (CB, 99% pure), and 1,2,4-trichlorobenzene (TCB, 99+% pure). Solutions of heptachlor, dieldrin, 1,2,4-trichlorobenzene and toxaphene were provided by the U.S. Environmental Protection Agency. Resi-analyzed grade n-hexane was purchased from J. T. Baker.

Procedure

1COA was chosen as the response standard due to its high purity and stability. Prepared solutions contained

1COA at concentrations of 589 nmol Cl/mL, 58.9 nmol Cl/mL or 5.89 nmol Cl/mL.

For construction of the calibration plot, solutions of TCPrA, DCPeA, CB and TCB were divided into two subsets and were measured by GC-HECD. Group I included 1COA, TCPrA and DCPeA; group II included 1COA, CB and TCB; the concentrations ranged between 7.8 nmol Cl/mL and 1.2×10^3 nmol Cl/mL.

Group I compounds were separated by a GC temperature program from $30^{\circ}C$ to $70^{\circ}C$, increased at $3^{\circ}C/min$ after a 5 min isothermal period at $30^{\circ}C$. For group II compounds separation was achieved with a temperature program from $30^{\circ}C$ to $75^{\circ}C$ at $4^{\circ}C/min$ after a 5 min isothermal period at $30^{\circ}C$. Solutions of toxaphene, dieldrin and heptachlor were eluted with temperature programming from $70^{\circ}C$ to $250^{\circ}C$ at $8^{\circ}C/min$ after a 2 min isothermal period at $70^{\circ}C$. A temperature program from $50^{\circ}C$ to $100^{\circ}C$ at $5^{\circ}C/min$ after a 4 min isothermal period at $50^{\circ}C$ was used for the 1,2,4-trichlorobenzene solution. Replicate chromatography measurements were made in order to calculate standard deviations.

All glassware used in dilutions and storage were acid-washed and hexane rinsed. Class A volumetric glassware, Eppendorf pipets and n-hexane were used for dilutions.

Instrumentation

A Tracor Model 560 gas chromatograph equipped with a Tracor Model 700A HECD was used. The column was 2 m x 2 mm I.D. silanized glass, packed with 3% OV-17 on 80/100 Supelcoport. Airco grade 4.5 helium was the carrier gas at 40 psi and Airco grade 4.5 hydrogen with a hydrocarbon trap was the HECD reactor gas, set at 20 mL/min. The conductivity solvent, n-propanol, was pumped at 0.5 mL/min. The nickel catalyst reactor temperature was $950^{\circ}C$, the HECD base temperature was $300^{\circ}C$, and the GC injector temperature was $250^{\circ}C$. Sample injection volumes were 0.4 μL and a Hewlett-Packard Model 3390A integrator measured the peak areas and retention times.

The flow control system (see page 13 and Fig. 11) included a Kurz Model 1541 mass-flow meter, a Rockwell AIM 65 microcomputer, a Porter VCD-1000 flow control valve, a Warner Electric Clutch and Brake Co. SM-024-0018 stepper-motor and digital electronics based upon a National Semi-conductor ADC-0817 analog-to-digital converter. The system is similar to a previous design (17). The mass-flow readout (FR) is monitored by the computer via the analog-to-digital converter. The computer compared the measured mass-flow with an operator-selected mass-flow value. The difference is then minimized via the computer by iterative adjustment of the stepper motor, which opens or closes the
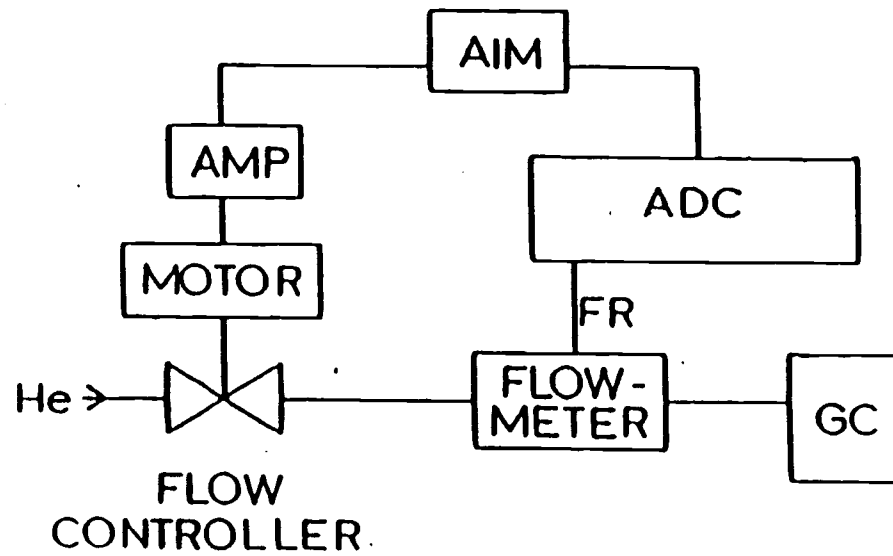
Fig. 11. Flow control system for constant mass-flow

flow control valve. Comparisons of FR and the desired flow value are repeated throughout each elution, with adjustments of the flow control valve made in response to nonzero differences between FR and the selected set-point. Outlet flows were measured with a bubble meter at ambient temperature in order to evaluate the mass-flow control system.

Results and Discussion

The mass-flow control system was able to maintain constant flow under diverse conditions. Figure 12 shows measured GC outlet flows obtained for the constant mass-flow system for isothermal conditions. Similarly, Figure 13 illustrates measured carrier outlet flows from the GC at an oven temperature of $50^{\circ}C$ for various mass-flow values. These figures demonstrate the ability of the flow control system to maintain constant flow over a range of oven temperatures and a range of mass-flow values. The periodicity of the deviations from constant flow shown in the figures is partially due to the pressure-relaxation time of the carrier gas, and partially due to pressure fluctuations in the pressure regulator used. Also, there is a short response time, about 1 sec, for the electronics and flow measurement systems' reaction to small deviations in flow.
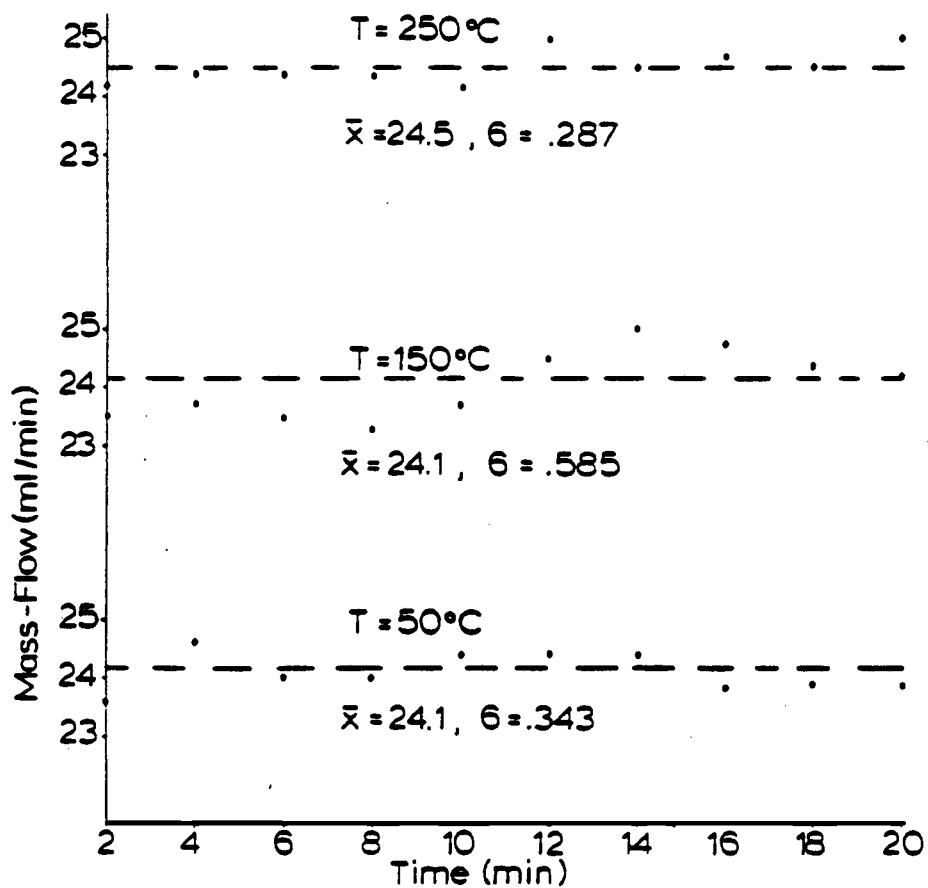
Fig. 12. Performance of constant mass-flow system for various isothermal conditions
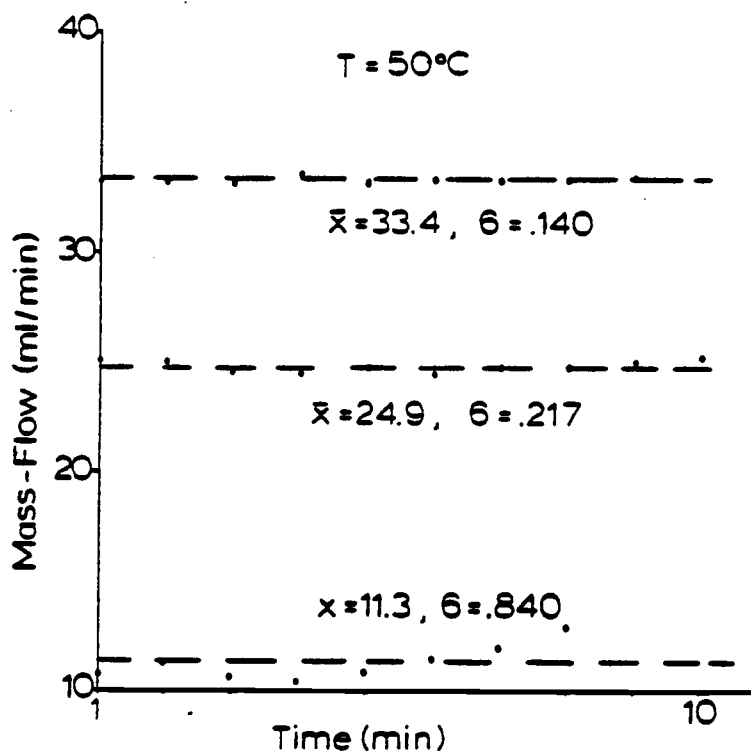
Fig. 13. Constant mass-flow system at various flow values

Comparisons of measured carrier flow during temperature programming using mass-flow control vs. without flow control (Fig. 14) demonstrates improvements resulting from use of the flow control system. The mass-flow control system maintained constant carrier gas flow with a relative standard deviation of less than 3% during temperature programming. Therefore the mass-flow of gas through the detector, which is kept isothermal, is constant if the reactor gas flow is constant and pressures are constant. Thus adverse effects on sensitivity due to variations in carrier gas flow are reduced. This is important for accurate measurements with concentration-dependent detectors for which sensitivity may change markedly with changes in flow. Detectors which respond to rate-of-analyte-delivery, such as the flame ionization detector, may also be affected by changes in carrier gas flow (18) and thus require constant flow conditions.

The results achieved with RFC and the HECD illustrate measurements which may be made with constant flow conditions. The response ratio, the analyte peak area (A_a) divided by the lCOA peak area (A_{rs}) (13), is linearly related to the μmol Cl/mL, since a calibration plot of log (μmol Cl/mL) vs. log (A_a/A_{rs}) had a slope of unity (Fig. 15). Linear least squares regression for the logarithmic calibration data (28 data) yielded an intercept $b_L = 1.188$
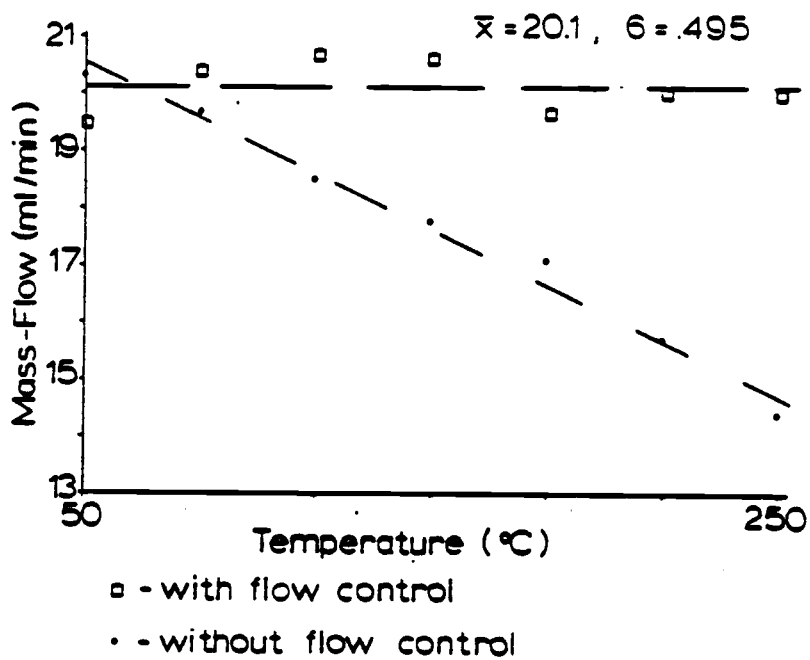
Fig. 14. Constant mass-flow system under temperature programming

$\pm$ .001 and a slope m = 1.063 $\pm$ .001. Thus detector re-
sponse is proportional to the eluates' organochlorine
content.

Analyte organochlorine concentrations, C_{Cl}, were cal-
culated as $C_{Cl} = (A_a/A_{rs})10^{-b}L$, using peak areas from the
chromatograms of dieldrin, heptachlor, 1,2,4-trichloro-
benzene, and toxaphene and each analyte's respective re-
sponse standard (1COA) peak. The results were calculated
in units of μmol of organochlorine per mL. Figure 16
shows typical chromatograms and corresponding concentra-
tions of measured impurities. The toxaphene solution (see
Fig. 17) was found to have a total Cl concentration of
57.48 $\pm$ .43 μmol Cl/mL (n=5). These quantitations were
achieved without identifications of each eluate nor the
use of reference substances identical to each analyte.

Constant flow is important for valid use of flow-sen-
sitive detectors. For the system described herein, sen-
sitivity of the detector was kept constant by maintaining
constant carrier gas mass-flow even during temperature
programming. This can be especially important for methods
which require sensitivity to be invariate during elutions,
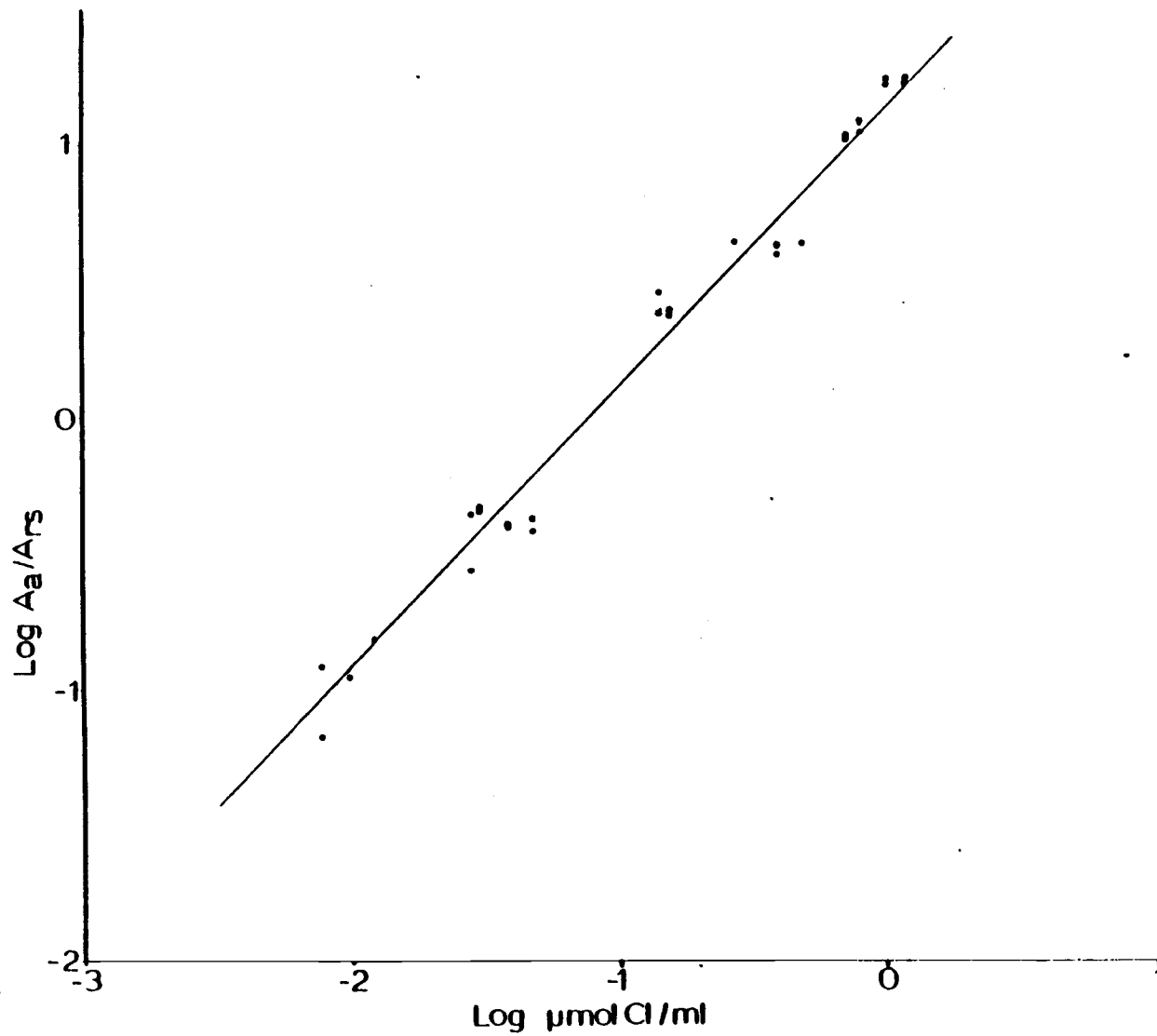such as RFC.

Fig. 15. Linearity of response ratio to organochlorine concentration

Fig. 16. Determination of impurities in EPA standards
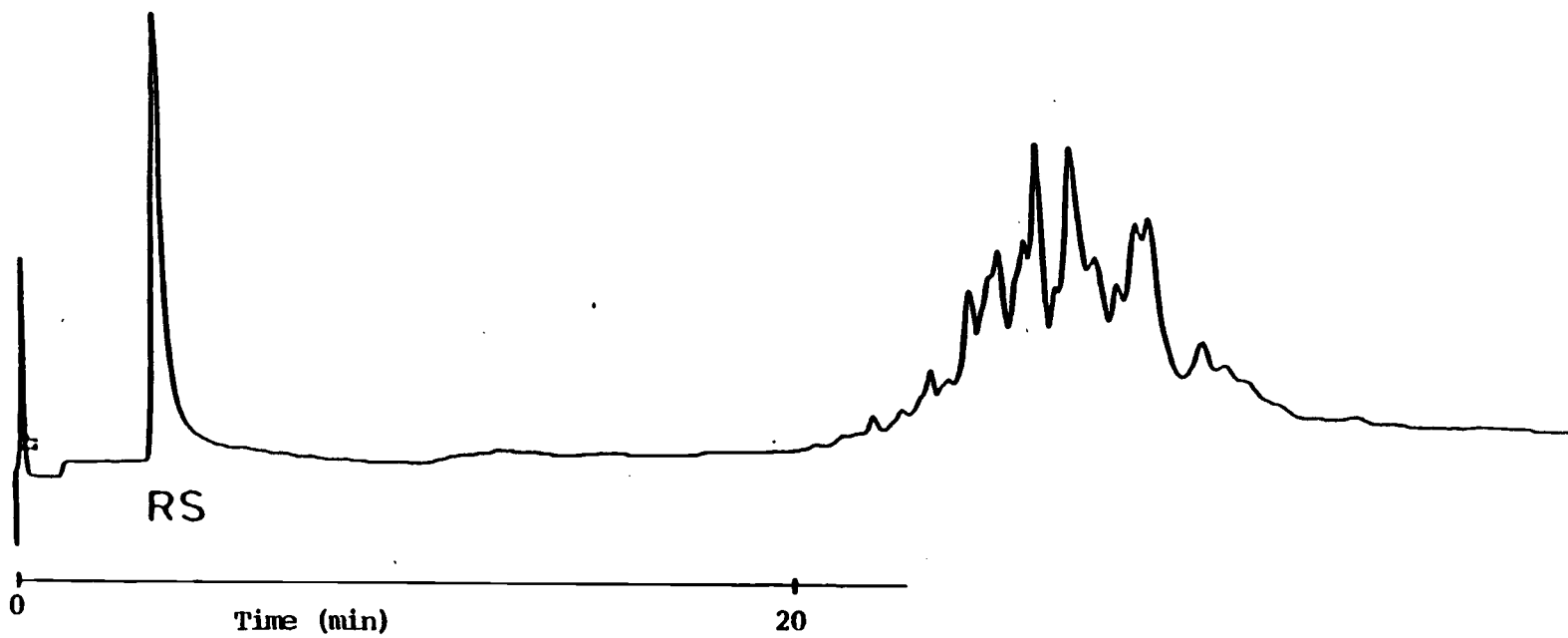
RS

0

Time (min)

20

Fig. 17.   Measurement of toxaphene

V. <u>SUGGESTIONS FOR FUTURE RESEARCH</u>

Figure 4 shows two difference-amplifiers in series which, in theory, may not be necessary. The AD-522B is a very good instrumentation amplifier but for unknown reasons was not able to perform adequate difference amplification. Future redesigning of the circuitry would include only the AD-522B should the problem in this circuit be solved.

Accurate quantitations using flow programming and an FID should be possible with this flow control system. Changes in carrier gas flow rate due to flow programming affect the response of the FID (18). By adjusting the make-up gas flow such that the total gas flow entering the detector remains constant throughout an elution, response can be kept constant. This could be done as a future project with this versatile system by using another flow meter and stepper motor to control the make-up gas flow. The AIM computer could be programmed to keep the sum of the gas flows from the column and make-up line constant.

It may be possible to improve the flow control system. One way to change the system would be to cause greater resolution of the needle valve, i.e., increase the number of steps per revolution of the value. This can be done by changing the gear ratio.

Exponential flow programming should be attempted with this system. It has been done in the past with capillary columns using pressure measurements, so this may be tried with a packed column.

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APPENDICES

APPENDIX A

MACHINE LANGUAGE SUBROUTINES

Assignment of Peripherals

Cell Location	Command	Comments
0D00	LDA #FF	Set apart B as output port
	STA A002	
	LDX #00	Set apart A as input port
	STX A003	
	INX	
	STX A00B	
	LDX #E9	Set peripheral control
	STX A00C	register
	LDA #00	
	STA A000	
	LDA A001	
	STA 0E00	
	LDA #02	Read oven temperature
	BIT A00D	
	BEQ 0D20	
	LDA A001	
	STA 0E00	Store over temperature value
0D2B	RTS	0E00 or 3584 in decimals

Reading the Flow

0C00	LDA #80	Read the flowmeter at the
	STA A000	ADC 0817
	LDA A001	
	STA 0E01	
	LDA #02	
	BIT A000	
	BEQ 0C0D	
	LDA A001	
	STA 0E01	Store the flow value at 0E01
0C18	RTS	or 3585 in decimal.

Stepping the Motor in the Open Direction

0D80	LDA #A9	
	STA A00C	
	LDA #00	
	STA A000	
0D8A	RTS	

Stepping the Motor in the Close Direction

```
ODC0            LDA #A9
                STA A00C
                LDA #01
                STA A000
ODCA            RTS
```

APPENDIX B

BASIC PROGRAM FOR OPTIMIZED FLOW PROGRAMMING
WITH TEMPERATURE PROGRAMMING

Line No.	Command	Comments
5	LET P=0	
10	POKE 4, 0:POKE 5,13	Go to subroutine at 0D00
12	T=USR (0)	
20	LET X=PEEK (3584)	Get temperature value
25	PRINT "TEMP= "; X	from 0E00
30	IF X < = 170 THEN $Y = 30.07 + .01367 X$	Calculate optimal flows in $^\circ$C and mL/min $Y = 8.58 + (3.672 \times 10^{-3}) (T)$
40	IF X > 170 THEN $Y = 1492 - 22.98X + 1145X^2 = (1.755 X 10^{-4}) X^3$	In $^\circ$C and mL/min, $Y = 416 - 6.594T + (3.403 \times 10^{-2}) T^2 - (5.452 \times 10^{-5}) T^3$
43	PRINT "OPT FLOW = "; Y	
45	If P > 1 THEN GOTO 75	
50	POKE 4, 0: POKE 5, 12	Go to subroutine at 0C00
60	LET Z = PEEK (3585)	First flow reading is at
65	PRINT "ZERO = "; Z	0 flow.
70	P = P + 1	
75	Y = Y + Z	
80	POKE 4, 0: POKE 5, 12	Read flow
85	T = USR (2)	
90	IF Y > 204 THEN $Y = 204$	Protection from trying to achieve too high of
95	LET F = PEEK (3585)	
100	IF F+Y THEN GOTO 10	
105	PRINT "FLOW = "; F	
100	IF F<Y THEN GOTO 130	
120	IF F>Y THEN GOTO 170	
130	POKE 4,128: POKE 5,13	Open the needle valve.
140	T=USR (0)	
150	PRINT "OPEN"	
160	GOTO 10	
170	POKE 4,192: POKE 5,13	Close the needle valve.
180	T=USR (3)	
190	PRINT "CLOSE"	
200	GOTO 10	
210	END	

APPENDIX C

CONSTANT FLOW PROGRAM

Line No.	Command	Comments
10	DIM Z (30)	
20	INPUT "FLOW VALUE (ML/MIN)"; F	Input flow value to be held constant.
23	POKE 4,0: POKE 5,13s	
25	T=USR (0)	
30	I=1	
40	FOR I=1 TO 20	Signal averaging of the
43	POKE 4,0: POKE 5,13	flowmeter output after
45	T=USR(0)	one full revolution of
50	POKE 4,0: POKE 5,12	the needle valve which
60	T=USR (1)	produces a He flow of
70	Z(I) = PEEK (3585)	3.16 mL/min.
80	NEXT I	
90	SUM=0	
100	FOR I=1 TO 20	
110	SUM=Z(I) + SUM	
120	NEXT I	
130	A = SUM/20	Average flow reading.
140	B = 3.16 - .2124A	Calculating Y-intercept
150	FOR I=1 TO 20	of linear eqa., line 50.
153	POKE 4,0: POKE 5,13	Signal averaging of the
155	T=USR (0)	present flow.
160	POKE 4,0: POKE 5,12	
170	T=USR (2)	
180	Z(I) = PEEK (3585)	
190	NEXT I	
200	SUM=0	
210	FOR I=1 TO 20	
220	SUM=Z(I) + SUM	
230	NEXT I	
240	X=SUM/20	Average flow reading
250	Y=.2124 X + B	
255	PRINT "FLOW = "; Y	
260	IF Y=F THEN GOTO 150	Compare inputed and
270	IF Y,F THEN GOTO 290	present flow values.
280	IF Y>F THEN GOTO 320	
290	POKE 4,128: POKE 5,13	Open flow valve.
300	T=USR(3)	
310	GOTO 150	
320	POKE 4,192: POKE 5,13	Close flow valve.
330	T=USR (4)	
340	GOTO 150	
350	END	

APPENDIX D

LIST OF ABBREVIATIONS

amp. - amperes

AC   - alternating current

A/D - analog-to-digital

ADC - analog-to-digital converter

A_a - analyte peak area

A_{rs} - area of response standard peak

cm   - centimeter

DC   - direct current

f_{opt} - flow rate optima

F   - farad

FID - flame ionization detector

FR   - flowmeter readout

GC   - gas chromatography/gas chromatograph

H   - theoretical plate height

HECD - Hall Electrolytic Conductivity Detector

HETP - height equivalent to a theoretical plate

I.D. - inside diameter

k   - kilo, 10^3

L   - liter

LSB - lease significant bit

MHz - megahertz

mL   - milliliter

mm   - millimeter

min   - minutes

mol   - moles

MSB   - most significant bit

n   - number of data

nmol   - nanomoles

O.D.   - outside diameter

p   - pico, 10^{-12}

p.s.i. - pounds per square inch

RFC   - response factor calibration

RSD   - relative standard deviation

sec.   - seconds

t_r - retention time

T   - temperature

TR   - oven temperature readout

V   - volts

W   - peak width at half-height

μ - micro, 10^{-6}

Ω - ohms

APPENDIX E

THE KURZ MASS-FLOW METER

DEVELOPMENTS IN
THERMAL FLOW SENSORS

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Over the years several thermal techniques have been used to measure the flow of fluids, and especially gases. Thermal sensors are commonly used to measure the mass flow rate when incorporated in flow bodies having a fixed geometry and to make velocity measurements in open spaces. Two basic types of thermal technologies are in use: energy balance and heat transfer.

The energy balance technique is primarily used for the measurement of mass flow rate. It assumes that the temperature gain of a fluid flowing through a tube is directly related to the mass flow rate and the heat capacity of the fluid. Generally, the technique requires long, small diameter tubes such that both the fluid mechanic and thermal profiles are fully developed. If, for example, the heat input is maintained constant, then the mass flow rate varies directly with the temperature difference. Generally, these types of flow meters have a linear output and are useful for very low flow rates. They can easily be calibrated for a variety of gases since the calibration is primarily dependent on the specific heat (Cp) of the gas. Because of the large length-to-diameter ratio requirement, these types of flow meter have a high pressure drop, are susceptible to clogging by foreign material and condensation, have a restricted linear rangeability, and generally have a slow time response.

The second type of flow sensor, described herein, is based on the heat transfer from a heated element to a flowing fluid. In most modern sensors, the sensor temperature is maintained as a constant temperature above the ambient temperature. The system is commonly referred to a as a constant temperature anemometer (CTA). It can be used as a velocity sensor or, if properly placed in a tube of known flow profile, it measures mass flow rate. This device responds to the local **mass velocity** or mass flow per unit area (SCFM/FT^2). It is generally considered to measure velocity when, in fact, it actually measures the product of density and velocity.

In using this device as a flow meter it is essential to condition the flow profile at the probe location such that the output is independent of upstream and downstream flow profile changes caused by elbows, valves, or even changes in flow rate. This can be accomplished through the use of adequate length, a flow nozzle and mixing screens. *Figure 1* shows a cross-section of a typical commer-
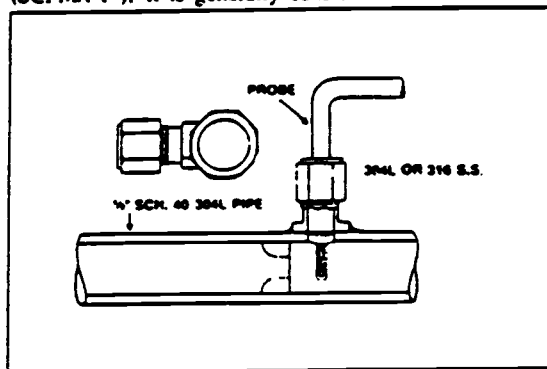

FIGURE 1

cial mass flow meter. The drawing shows that there are two sensors. R_p and R_{TC}. R_p is the velocity sensing element which is maintained at a constant temperature. R_{TC} is an ambient temperature sensor and is used in a bridge circuit with R_p to fully compensate for changes in gas temperatures. Because the constant temperature anemometer is based on heat transfer from a heated element, and not all of the fluid passing through the flow

body is uniformly heated, the output is a non-linear function of the mass flow rate and is related to the several fluid properties instead of only the specific heat. Thus, calibration in one fluid cannot usually be simply related to other gases, and special calibrations are needed. This type of mass flow meter has several outstanding advantages. It has exceptional flow rangeability (up to 500:1), which means that one size can be used to replace several transitional flow meters. Because of the "open-flow" characteristic, there is little chance for flow obstruction, and the pressure drop is extremely low (usually less than 2" of H$_2$O, dependent on design). This low pressure drop feature is essential when such units are used for on-site flow calibrations of air pollution sampling equipment, for example. Through the use of electronic linearization, a linear output is available. Another feature of this design is the fast response to changes in flow. Even large devices have a time constant of about .01 seconds. With the use of the linearization circuit and an integration circuit, extremely accurate measurements can be made in flow situations having pulsating flow or large changes in flow. This feature is particularly useful for use as a breath flow meter, for example.

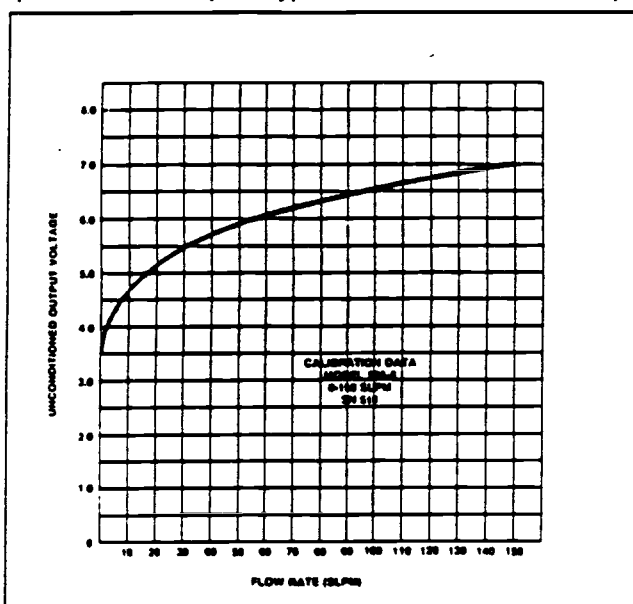The same advantages apply to its use as a velocity sensor in ducts, stacks, and open spaces. The sensitivity of a typical thermal anemometer is exceptional as can be seen in Figure 2. Instead of an output signal in the millivolt range, as in energy balance flow meters, this device has a large, healthy signal level of several volts, normally between about 3.5 VDC at zero flow to about 10.0 VDC at full scale flow. Thus, expensive amplifiers are not needed for signal conditioning.

In the past, most thermal anemometers have used the so-called "hot-wire" sensor, which is very small (from about 0.2 mil to 6 mil diameter). The

FIGURE 2

fragility of these sensors and their related susceptibility to dirt and resulting calibration shift has previously greatly discouraged the use of the "hot-wire" technique for industrial and environmental applications. The development of large, rugged probes has allowed the use of this type of sensor in a variety of industrial applications. The sensors are constructed of reference grade platinum, ceramic and are glass coated; they are identical to the construction specified by NBS for their standard resistance temperature sensor. The repeatability of the sensor is unsurpassed. The larger sizes (.032"-.125d") of the velocity sensor allows the sensor to operate in extremely dirty environments with little effect on the calibration. This is true because the impaction parameter relating to the size

of particles which are capable of striking and sticking to large sensors is several orders-of-magnitude lower than for the small diameter "hot-wire". Because of the relatively thin layer of contamination which may coat a sensor in this environment compared to the size of the sensor, because the flow field is only slightly affected, and due to the very low operating temperature and heat flux at the sensor su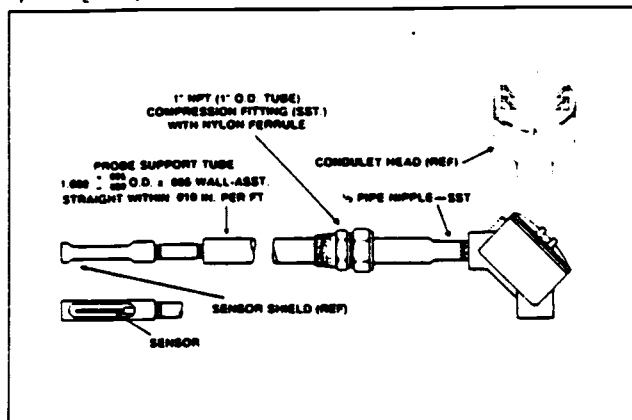rface, the calibration is very slightly affected by operation in dirty environments. Because the sensor is large and rugged it can be easily cleaned. As a practical example, Kurz Instruments, Inc., sells a stack velocity system to monitor the mass flow rate in copper smelter stacks with excellent success. *Figure 3* shows a drawing of this probe.

FIGURE 3

It is important to understand that thermal sensors, if properly temperature compensated, measure mass flow rate and not volumetric flow rate. Mass flow rate is generally the preferred unit of measurement in flow metering, combustion measurements, air sampling, energy management, etc. Modern thermal anemometers can be made rugged, reliable, repeatable, and highly accurate for a wide range of conditions. Therefore, secondary measurement of pressure and temperature is not required to correct the output as is needed in all volumetric or differential pressure flow meters. This is a great saving in cost, considerably reduces installation time and improves accuracy.

The development of a 2-wire current-mode anemometer transmitter has been a major advancement in the industry. This feature allows operation with cable length independence, reduces installation time and eliminates electromagnetic intereference (EMI). An additional feature is direct interchangeability of flow transducers which simplifies operation and has the potential of greatly expanding the industrial use of thermal sensors. The fast response makes the CTA an ideal candidate for process control systems. These systems have been used for constant mass flow control of pumps, fans and blowers; for constant velocity systems in clean rooms, automatic isokinetic sampling of gases and particulates in environmental measurement, and in gas blending systems. Recently a system for leak testing has been developed in which a mass flow control system is used to maintain a constant test pressure to the test device. In this case a thermal mass flow meter is used to sense pressure drop by the maintenance of a constant mass flow rate through a fixed orifice.

As is true of all inferential type mass flow sensors, the calibration of thermal sensors is affected by gas composition. Thus, a system calibrated in air will be affected by humidity, for example. Generally these effects are minor for normal atmospheric conditions. However, in combustion stacks, drying applications, or in situations where the fluid composition may drastically change, it is important that these effects be accounted for, or eliminated. One solution is to establish correction charts for common gas mixtures. This is being worked on at the present time.

Kurz Instruments, Inc., noticed that in most situations requiring total mass flow in a stack or duct, a gas or particulate sample is also required. Generally, it is required to obtain an isokinetic or proportional sample in order to obtain a representative sample of particulate. We recognized that if both the sample flow rate and the stack gas velocity were measured simultaneously in the stack, and if both sensors were constructed identically and operated at the same temperature, a system could be used to control the flow rate of the extracted sample. Th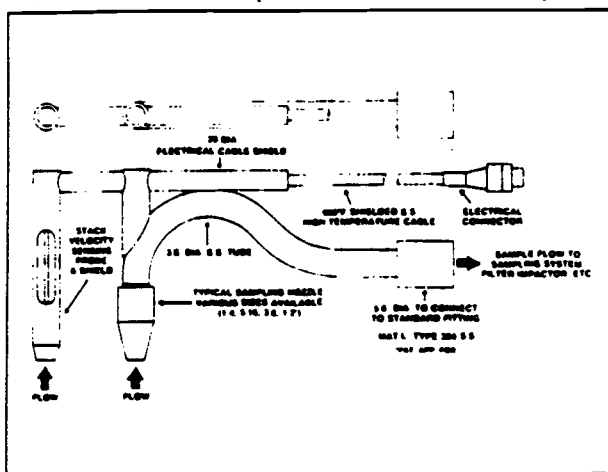en the extracted sample could be dehumidified and measured using a dry gas meter. Thus, measurements of particulates and gases can be referenced to dry gas conditions as is required by the EPA, for example.

FIGURE 4

Figure 4 shows a picture of the automatic isokinetic sampler sensor assembly. Both sensors are maintained at a constant temperature. Because the sampling nozzle also functions as the mass flow meter nozzle, the velocity in the sampling nozzle is identical to that of the velocity sensor at isokentic conditions. An electronic flow control valve is used to sense the voltage difference between the two sensors and adjust the flow rate to obtain a balance. Thus, the system operates as a differential device, and is independent of gas composition and temperature. Once the equivalent dry gas flow rate has been determined, all other parameters may be calculated by using the sample nozzle area and the stack area.

In summary, a lot of exciting improvements have been made to thermal sensors over the last few years. We believe the modern thermal anemometer will add greatly to our measurement capabilities and become an important addition to industrial and process instrumentation.

J.L. Kurz
May, 18, 1982

SPECIFICATIONS

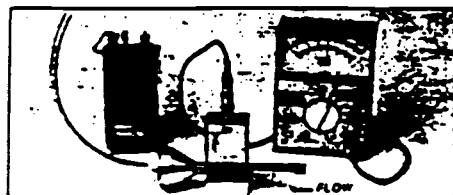| Model Number	540S	541S	543	544
Flow Ranges (SLPM)	0-0.05	0-0 05	0-2	0-5
(referenced to 25°C and	0-0.2	0-0.2	0-10	0-15
760 mm Hg)	0-1.0	0-1.0	0-50	0-50
	0-3.0	0-5.0		0-150

Accuracy of Flow Measurement	±2% of full scale for each flow range over a temperature range of -20°C to +60°C and a pressure range of .25 to 2 atmospheres (applicable above 10 sccm)
Repeatability	±0.25% of full scale for each range
Temperature Ranges	Transducer: -55°C to +125°C, Meter: 0°C to 50°C
Response Time	Transducer: .1 second; Meter Readout: .5 second
Maximum Pressure Drop	4.5 cm H₂O high range (1.8 in H₂O) 0.18 cm H₂O mid-range (.07 in H₂O) 0.007 cm H₂O low ranges (.003 in H₂O)
Pressure Range of Transducer	500 psi (accuracy guaranteed to 30 psi)
Power	Nickel-cadmium battery with 115/230 VAC, 50/60 HZ charger, operates up to eight hours between charges
Net Weight of Meter and Transducer	1.25 Kg/ 2.75 lb.
Shipping Weight	2.3 Kg/ 7 lb.
Meter Readout	Custom, ruggedized, self-shielding 11.5 cm taut-band mechanism, self-storing handle, shock-proof
Flow Transducer Material	Nickel-plated aluminum and lexan flow body; ceramic, platinum and epoxy sensors; stainless steel available
Transducer Dimensions	2.54 cm x 8 cm x 5.32 cm, ¼" NPT female inlet and outlet, except for 544 with ¾" NPT, male threaded, 10" long
Controls	Mechanical zero on meter face, zero and span controls inside meter, range and battery test switch on front panel
Dimensions	Meter: 2" x 5" x 7"; Carrying Case: 3" x 10" x 14"
Analog Output Option	0-1 VDC corresponding to the high flow range, non-linear data supplied. Add "-A" to model number when ordering
Filter Cassette Adapter Options (All models except 544)	Allows direct attachment to standard 37 mm cassettes (add "-B" to model number), or 47 mm cassettes (add "-F" to model number)
Pre-filter (47mm) Cassette	Eliminates wind affects when calibrating virtual impactors. Add "-C" to model number when ordering
Retractable Cable Option	Six feet of retractable cable (11 inches when coiled) replaces standard 15 foot cable. Add "-R" to model number
Stainless Steel Option	Add "-SS" for 304 stainless steel flow body Add "-SS(316)" for 316 stainless steel body
Digital Bench Model	Ask for Digital Bench Cabinet brochure Models (545-1, 545-2, etc.)
Warranty	1 full year parts and labor

Calibration of Personal Sampling Pump
shown with "B" Cassette Adaptor Option

Typical Meter Scale Model 541S
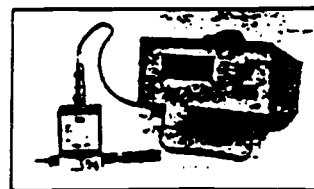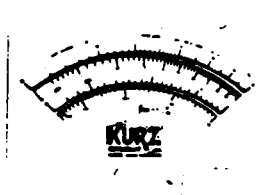
Optional Model 545-1 Digital
Display Bench Cabinet

APPENDIX F

RESPONSE FACTOR CALIBRATION

RFC methods allow for quantitative measurements with-
out eluate identification nor the need for pure reference
substances for each)analyte. Quantitative procedures in
chromatography generally require that pure reference
substances be available for all measured eluates, from
which instrumental response factors can be obtained for
each analyte to be determined. Typically, exploratory
determinations begin with analyte identifications which
can be time consuming, or require expensive instruments
and experienced technicians. Once analytes are identi-
fied, appropriate reference substances must be obtained
via purchase, synthesis, or purification from natural
origin. Such procedures must be carried out before reli-
able quantitation can be assured, unless the instrumental
response factor for each analyte can be otherwise ob-
tained.

Alternatively, response factor relationships are
sometimes assumed. For example, in determinations by GC-
MS it is sometimes assumed that sensitivities are virtual-
ly the same for structurally related compounds, although
the assumption may be invalid. However, such an assump-

tion can be appropriate for selected measurements, as described below.

Reliable pure standards are often not available for various reasons, e.g., compound instability, expense, tedious syntheses, or purification complications. Despite the absence of reliable reference substances, such compounds may still need to be determined because of their economic importance, environmental persistence, suspected toxicity or involvement in important metabolic pathways. Therefore, alternatives to methods requiring identification of, or pure reference substances for, each analyte should be useful.

Response factor calibration (RFC) is one such method (12). It allows for quantitations of substances without the need for compound identification nor the need for acquiring identical reference materials for each measured analyte. Presently, analytes are typically measured by chromatography using standard additions, external standard, or internal standard techniques; each of these techniques requires a reference substance identical to each analyte to ensure accurate quantitations.

Typically, chromatographic quantitations use either external (ES) or internal standard (IS) methods. Those procedures require analyte identification and availability of proper reference compounds. Also, both procedures

require comparisons of measured responses to reference chromatograms, either via ratios or an assumption of a constant response factor for IS and ES methods, respectively.

Conventional methods which necessitate identical reference compounds may be preferred but they may not always be feasible for important analyses. Therefore, methods which do not require identical reference substances, e.g., RFC, are needed.

When identical reference substances are not available, response factors may be assumed for individual analytes, usually based upon response factors for similar compounds. Although this assumption is generally invalid for systems such as GC-MS and GC-EC it sometimes allows for reasonable estimates even when identical reference substances are not available. However, identifications of the analytes are needed in order to invoke the similarity assumptions.

RFC avoids requirements of analyte identification and availability of reference substances identical to each analyte: it allows for accurate measurements without identification of the analytes, and does not require reference compounds which are identical with each analyte. RFC methods depend upon modification of analyte components to a common measured species (12). If the measured spec-

ies' response factor, or sensitivity, is independent its analyte source, then its response factor may be constant for all analytes during a measurement interval, e.g., a chromatographic elution. A response standard (RS) of known composition may therefore be used to calibrate the measured species' response factor.

Thus, RFC procedures calibrate the response of a measured species during each elution, thereby avoiding interelution dependencies. Moreover the calibration substance, or response standard (RS), is the only analyte for which identity and availability of a pure reference material must be ensured.

The RFC methods could be especially advantageous in determinations of analytes in complex samples such as environmental samples or samples from toxicologic studies. Analytes of unknown identity are encountered often in such complex samples, and identified analytes for which identical reference substances are unavailable may also be found. For example, individual polychlorinated butadienes (PCBD's) may be detected and sometimes identified by GC-MS but their reference solutions usually cannot be stored in pure form, are difficult to synthesize, are unavailable, or are prohibitively expensive. Moreover, attempts to quantitate PCBD reaction products are hindered by a lack of knowledge of their identities or by unavailability of

reference compounds for the many possible PCBD reaction products. There are many compounds which pose difficulties similar to those shown by PCBDs and PCBD reaction products. RFC does not require identification of analytes nor acquisition of identical reference compounds for each analyte. Therefore, it could be useful for such analytes, for which quantitative measurements are presently precluded or unreliable.

The RFC method could be generalized for use with detection systems other than the HECD. RFC requires that: (a) the detector response factor for the measured species be independent of the analyte, (b) the response factor vs. concentration relationship for the measured species be unambiguous, and (c) the response factor for the measured species remain constant over the duration of measurements for the analyte and a response factor standard. Chromatography systems may require additional restrictions for valid use of RFC, such as constant flow during the measurements and sufficient resolution of eluates. The prospect for applying RFC to measurement systems other than GC-HECD is promising, and could be valuable in studies needing otherwise intractable quantitations.

The Hall electrolytic conductivity detector (HECD) fulfills the requirements for use of RFC. Its response, relative to a response factor standard, is directly

related to the concentration of organically bound chlorine
for chlorinated hydrocarbons.   HECD detector response to
known concentrations of chlorinated hydrocarbons, relative
to the response factor standard, were colinear when
graphed versus analyte organic chlorine concentrations.
The response factor standard acts as a detector response
reference for all determined eluates, similar to an
internal standard, but it requires neither analyte
identification nor identical reference substances for each
analyte determined. Moreover, all information for quanti-
tative calculations are found in each individual chromato-
gram.

The response factor calibration method has several
quantitation levels. The basic quantitation requires
detector response calibration data for analyte determina-
tions.   Each other level requires additional information,
such as supplemental GC-MS data.   As an example, several
chlorinated hexachlorocyclopentadiene photolysis products
were determined by using the four quantitation levels of
the RFC with HECD detection and GC.   Other detectors
should be compatible with RFC.