Note

Constant mass flow system for gas chromatography

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The sensitivities of concentration-dependent gas chromatographic (GC) detectors are related to the gas flow through the detector[1]. 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 Hall electrolytic conductivity detection (HECD) is one quantitative method which requires constant-flow conditions[2].

To fulfill the constant sensitivity requirement, instrumentation to provide constant flow was developed. It was used with the RFC method to measure chlorinated compounds with a Hall electrolytic conductivity detector operated in the halogen mode. For RFC, analyte response relative to a response standard must be proportional to the amount of organochlorine eluted[2]: HECD is consistent with this requirement[2–4]. Quantitative measurements were made of toxaphene and of impurities in solutions of dieldrin, heptachlor and 1,2,4-trichlorobenzene. These determinations were achieved without analyte identifications nor pure reference compounds for each measuured eluate.

Constant mass flow of the carrier gas into the GC column inlet was maintained via mass flow measurements and computer-controlled flow adjustments. Possible decreases in flow of the carrier gas at the column outlet relative to the inlet during temperature programming[5] were not significant in this work. Although temperature programming was necessary to achieve separations for these analyses, the flow control system maintained constant carrier gas mass flow during elutions. Thus flow through the isothermal detector was constant, resulting in constant detector sensitivity required by GC methods such as RFC.

EXPERIMENTAL

Reagents

Reference substances were purchased from Aldrich Chemical: 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. Resianalyzed 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 $1.2 \cdot 10^3$ nmol Cl/ml.

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

All glassware used for 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 Hall electrolytic conductivity detector was used. The column was 2 m × 2 mm I.D. silanized glass, packed with 3% OV-17 on 80/100 Supelcoport. Airco grade 4.5 helium was the carrier gas 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°C, the HECD base temperature was 300°C, and the GC injector temperature was 250°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 Fig. 1) included a Kurz Model 1541 mass flow meter, a Rockwell AIM 65 microcomputer, a Porter VCD-1000 flow control valve, a Warner Electric Cluth and Brake Co. SM-024-0018 stepper-motor and digital electronics based upon a National Semiconductor ADC-0817 analog-to-digital converter. The system is similar to a previous design[6]. The mass flow readout (FR) is monitored by the computer via the analog-to-digital converter. The computer compared
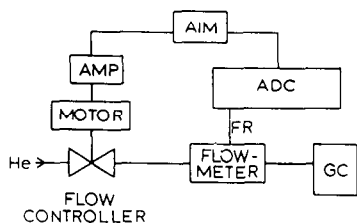

Fig. 1. The mass flow control system for maintaining constant carrier gas flow.

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 via the amplifier (AMP), which opens or closes the 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 non-zero 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. Fig. 2 shows measured GC outlet flows obtained for the constant mass flow system for isothermal conditions. Similarly, Fig. 3 illustrates measured carrier outlet flows from the gas chromatograph at an oven temperature of 50°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 system's reaction to small deviations in flow.

Comparisons of measured carrier flow during temperature programming using mass flow control vs. without flow control (Fig. 4) 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-depen-
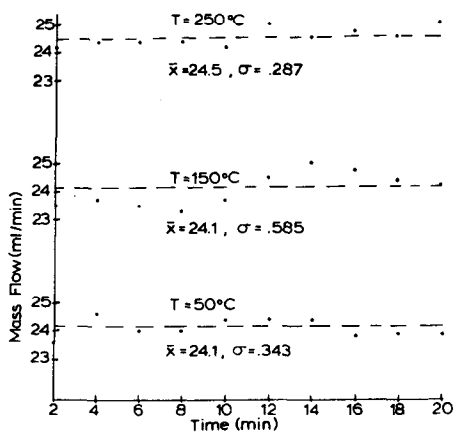

Fig. 2. Measured carrier gas flow vs. time with the system maintaining constant mass flow for isothermal conditions.
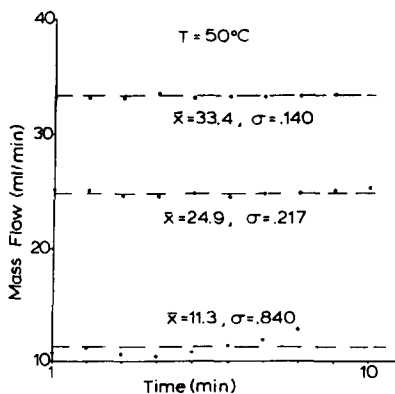
Fig. 3. Measured carrier gas flow vs. time with the system maintaining different constant mass flow values.
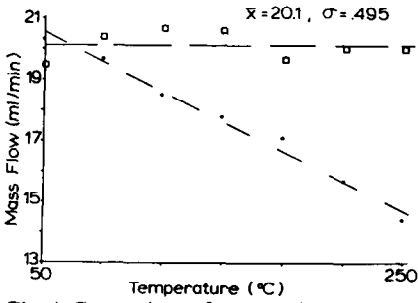
$\bar{x} = 20.1$, $\sigma = .495$

Fig. 4. Comparison of measured carrier gas flows with and without constant mass flow maintained by the flow control system for temperature program conditions: temperature program was from 50°C to 250°C at 5°C/min. □ = With flow control; . = without flow control.

Dieldrin

peak #	Cl ($\frac{\mu mol}{ml}$)
1	0.497 ± 0.069
2	0.135 ± 0.032
3	0.507 ± 0.184
4	0.102 ± 0.021
5	0.035 ± 0.002

1,2,4-trichlorobenzene

peak #	Cl ($\frac{\mu mol}{ml}$)
1	0.229 ± 0.097
2	0.113 ± 0.026

Heptachlor

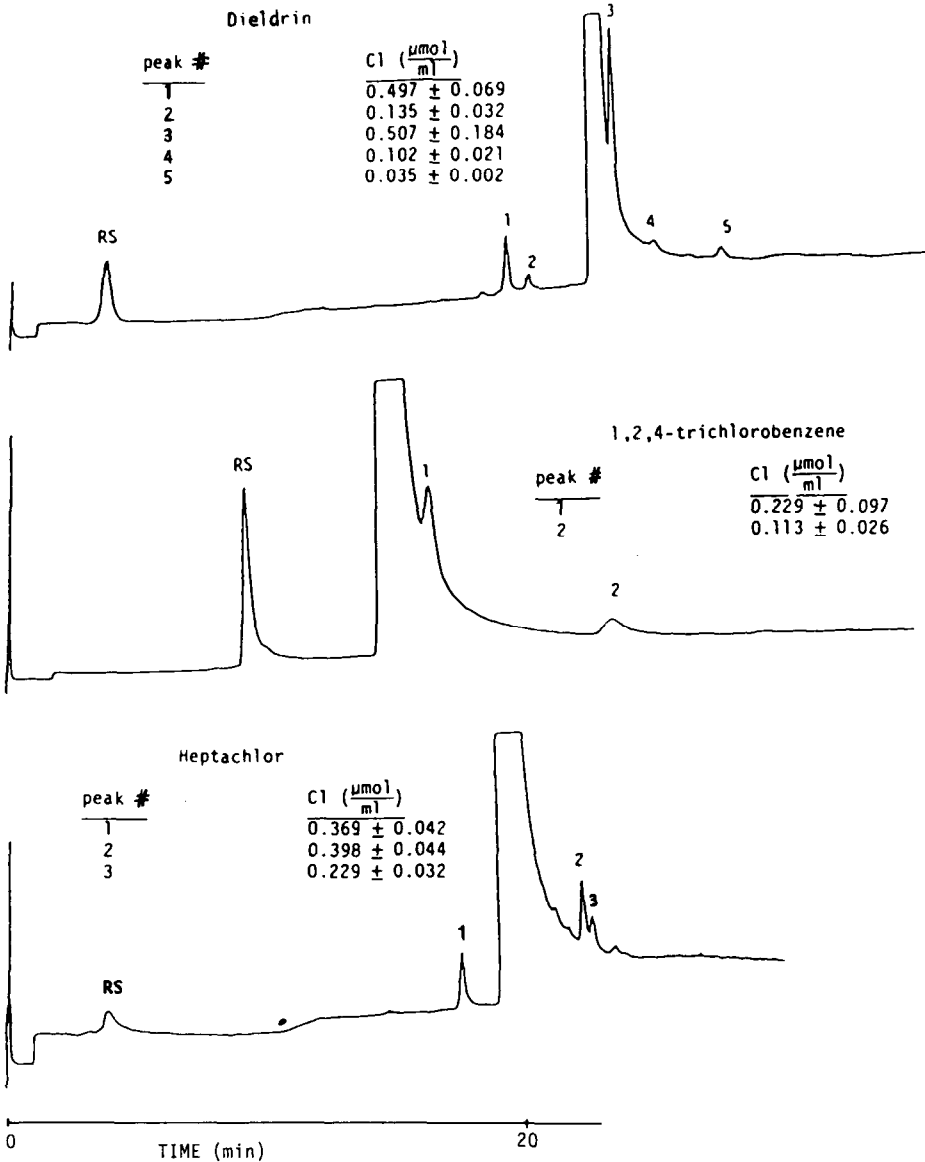| peak #	Cl ($\frac{\mu mol}{ml}$)
1	0.369 ± 0.042
2	0.398 ± 0.044
3	0.229 ± 0.032

TIME (min)

Fig. 5. Typical chromatograms for EPA standard solutions with constant mass flow and temperature programming. Listed concentrations are for quantitations of the respective impurities, RS = response standard, $n = 4$.

dent 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[7] and thus require constant flow conditions.

The results achieved with RFC and HECD illustrate measurements which may be made with constant flow conditions. The response ratio, the analyte peak area (A_a) divided by the 1COA peak area (A_{rs}) (ref. 2), 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. Linear least squares regression for the logarithmic calibration data (28 data) yielded an intercept, $b_L = 1.188 \pm 0.001$ and a slope, $m = 1.063 \pm 0.001$. Thus detector response is proportional to the eluates' organochlorine content.

Analyte organochlorine concentrations, C_{Cl}, were calculated as $C_{Cl} = A_a/A_{rs}$ 10^{-b_L}, using peak areas from the chromatograms of dieldrin, heptachlor, 1,2,4-trichlorobenzene and toxaphene and each analyte's respective response standard (1COA) peak. The results were calculated in units of μmol of organochlorine/ml. Fig. 5 shows typical chromatograms and corresponding concentrations of measured impurities. The toxaphene solution (see Fig. 6) was found to have a total Cl concentration of 57.48 ± 0.43 μmol Cl/ml ($n = 5$). These quantitations were achieved without identifications of each eluate or the use of reference substances identical to each analyte.
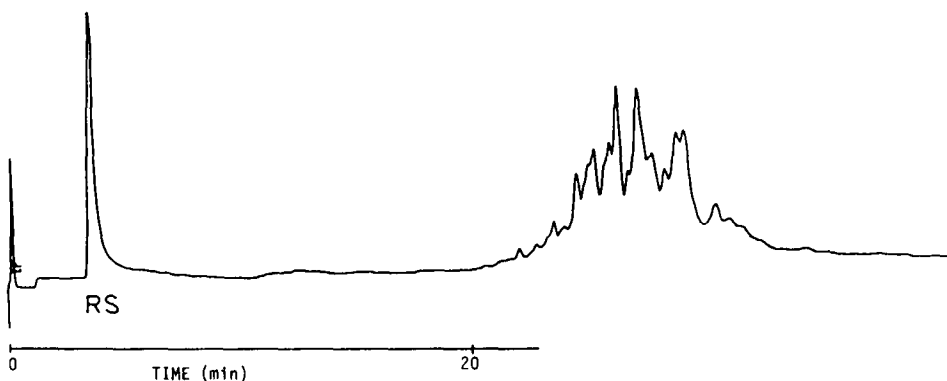

Fig. 6. Chromatogram for a toxaphene solution achieved with constant mass flow control and temperature programming. RS = Response standard.

Constant flow is important for valid use of flow-sensitive detectors. For the system described herein sensitivity 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.

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