Journal of Chromatography, 158 (1978) 465–469

CHROM. 11,119

RAPID EVAPORATION OF CONDENSED GAS CHROMATOGRAPHIC FRACTIONS

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SUMMARY

A low-volume cold-trap is described that can be used to condense fractions eluted from a gas chromatographic column and subsequently to vaporize the condensed fraction into another column within 20 msec by means of an electrical heater circuit.

INTRODUCTION

An important stage in multi-dimensional gas chromatography is the condensation of particular fractions eluted from a column and the subsequent evaporation of these fractions into another column[1,2]. The cold traps used for this purpose serve as inlet devices and must fulfil the functions of a well designed inlet. Basically, this implies that the sample should be delivered to the column as a plug with a bandwidth that is sufficiently narrow not to detract significantly from the inherent column performance. A thorough fundamental study of such traps is still lacking; however, factors that would play a role in determining the sample inlet bandwidth are the way in which the sample is condensed, the geometry of the trap and the mode of evaporation of the sample.

Traps usually consist of a short length of narrow-bore metal tubing and condensation of the sample is effected with a jet of nitrogen that has been cooled by passage through liquid air. Evaporation is achieved with a jet of heated nitrogen. The low heat capacities of the gases lead to relatively slow evaporation rates, which, in certain circumstances, can significantly affect the column performance. In this paper we describe a method of electrically heating the trap.

THEORETICAL

Consider a cold-trap connected between two columns as shown in Fig. 1. The width of the band condensed in the trap, w_t, is determined by the average linear flow velocity in the trap, $\bar{u}_t$, and the time taken by the solute molecules in the vapour phase of the trap to diffuse to the cold wall, t_D. (We assume that the condensation occurs at a single collision with the cold wall.) Thus,

$$w_t = \bar{u}_t t_D \tag{1}$$

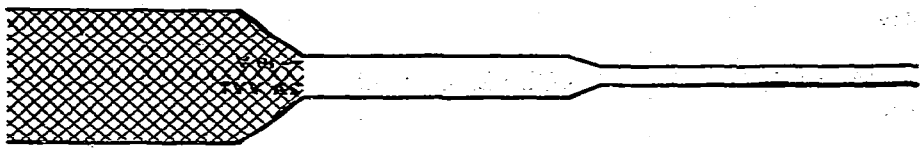

Fig. 1. Geometry and operating conditions of cold trap and columns:

	Column 1	Trap	Column 2
Average linear flow velocity	$\bar{u}_1$	$\bar{u}_t$	$\bar{u}_2$
Radius	r_1	r_t	r_2
State	packed	open tube	open tube

As

$$t_D = \frac{r_t^2}{8D} \tag{2}$$

from the Einstein diffusion equation and

$$\bar{u}_t = \frac{r_1^2}{r_t^2} \cdot 0.4\bar{u}_1 \tag{3}$$

it follows that

$$w_t = \frac{0.4\bar{u}_1 r_1^2}{8D} \tag{4}$$

If, typically, we assume $r_1 = 3$ mm, $D = 10^{-1}$ cm^2·sec^{-1} and $\bar{u}_1 = 5$ cm·sec^{-1}, then

$$w_t = \frac{0.4 \cdot 5 \cdot (0.3)^2}{8 \cdot 0.1}$$

$$= 0.2 \text{ cm}$$

The width of the sample leaving the trap, w_t^0, is determined by w_t, the time taken to vaporize the sample, t_v, and the average linear flow velocity in the trap. Thus,

$$w_t^0 = w_t + t_v\bar{u}_t \tag{5}$$

$$= \frac{\bar{u}_1 r_1^2 \cdot 0.4}{8D} + \frac{t_v r_1^2 \cdot 0.4\bar{u}_1}{r_t^2} \tag{6}$$

The width of the sample entering column 2 is

$$w_2 = \frac{w_t^0}{1+k} \cdot \frac{r_t^2}{r_2^2} \tag{7}$$

where k is the partition ratio of the sample. The contribution of w_t to the plate height of column 2 is negligible if

$$w_2 < \tfrac{1}{4}(LH_c)^{\frac{1}{2}}$$

where L is the length of column 2 and H_c is the plate height of column 2.

If, typically, we ascribe values of $L = 100$ m, $H_c = 0.03$ cm, $k = 2$ and $r_t = r_2 = 250$ μm, it follows from the above equations that

$$w_2 < 4 \text{ cm}$$

$$w_t^o < 12 \text{ cm} > w_t \approx 0.2 \text{ cm}$$

The contribution of the condensation step should therefore be negligible.

From eqn. 6, it follows that the heating time of the trap, t_v, is given by

$$t_v < \frac{12 r_t^2}{r_1^2 \cdot 0.4 \bar{u}_1}$$

$$\approx \frac{12 \cdot 6 \cdot 10^{-4}}{9 \cdot 10^{-2} \cdot 0.4 \cdot 5}$$

$$\approx 40 \text{ msec}$$

If the cold trap is constructed from stainless steel (5.5 cm long, 250 μm I.D., 500 μm O.D.), its mass is approximately $6 \cdot 10^{-2}$ g and it would need *ca.* 6 J to heat it from −180 to 300°. If heated nitrogen, at say 800°, were used for this purpose, approximately 375 ml·sec^{-1} of gas would have to contact the trap. This is clearly difficult, and electrical heating of the trap was considered as an alternative. From the data in the previous paragraph it is estimated that 125 W would be required to heat the tube from −180 to 300° in 40 msec. The circuit designed for this purpose was required to heat the tube in 20 msec.

APPARATUS

Heating circuit (Fig. 2)

The solid-state relays SSR1 and SSR2 (Elec-Trol PNSA 10094225 and PNSA 10094210, respectively) consist of triacs driven by a zero-crossing detector controlled by a light-emitting diode (LED) isolated input. When a TTL (transistor–transistor logic) level signal is applied to the control input, the triac will switch on at the next zero-crossing of the mains cycle. The welding transformer primary can thus be switched on to either the 20-A variable voltage transformer (VVT) set at about 180 V for rapid heating, or to the 2-A VVT set at about 10 V for maintaining the chosen temperature. The remainder of the circuit ensures that the relays cannot be activated simultaneously and allows for only a 10-msec pulse of the 185 V, *i.e.*, half a cycle.

The cross-connected NAND gates (G1, G2) act as a Set–Reset Flip-Flop and together with the control buttons, determine the state of the circuit. On pressing Reset, point A goes low and both relays are held off. When Start is pressed point A changes to a high value and point B goes low for 9 msec, which is set by the 10 kΩ variable resistance. This actuates SSR1 for 9 msec and holds off the other SSR. After one half-cycle of 185 V is pulsed into the welding transformer and the monostable multi-vibrator (Texas Instruments, 74121) 9 msec period has elapsed, SSR1 goes off and SSR2 comes on, switching the 10 V through to the welding transformer thereby maintaining the trap temperature at the chosen value. The LED also switches on, indicating the On state. The 74121 period is adjusted to slightly less than the

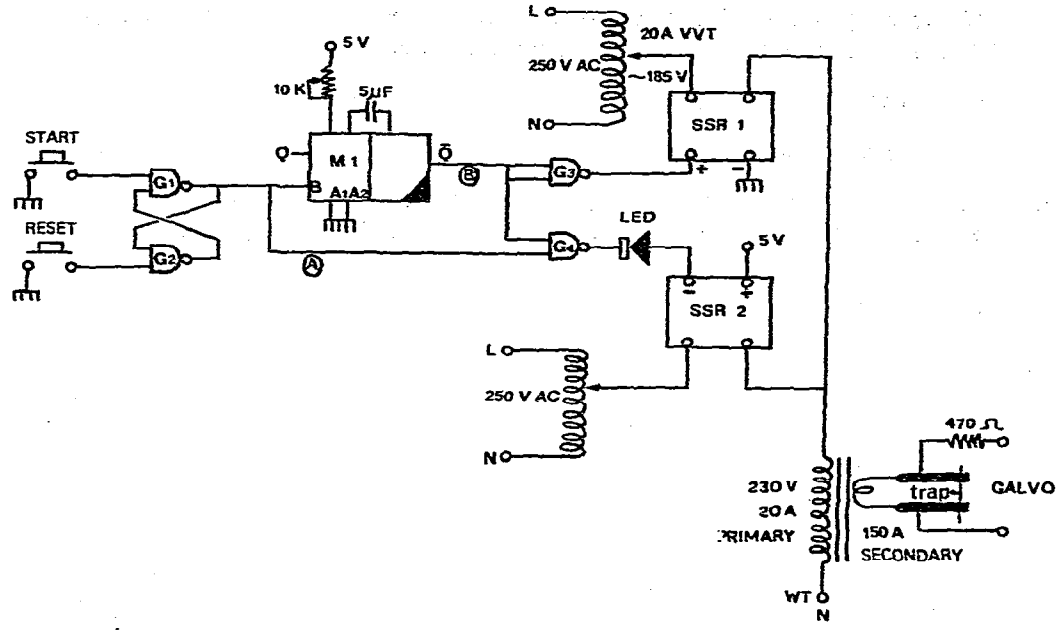

Fig. 2. Heater circuit.

mains half-cycle time. The 2-A VVT is adjusted to give the steady-state temperature required and the 20-A VVT is set to give the chosen temperature jump.

The trap is connected to the 14-A secondary of the welding transformer by means of 0.5-in. aluminium bars.

Temperature-measuring circuit (Fig. 3)

The temperature of the trap is measured by its emitted radiation. A photo-transistor, PT (Texas Instruments, 2N 5777), sensitive to infrared radiation in the range 0.5–1.0 μm, is connected to a 100-Hz galvanometric recorder (Visigraph) as shown in Fig. 2, via an amplifier, A (Texas Instruments, 741), as is shown in Fig. 3.

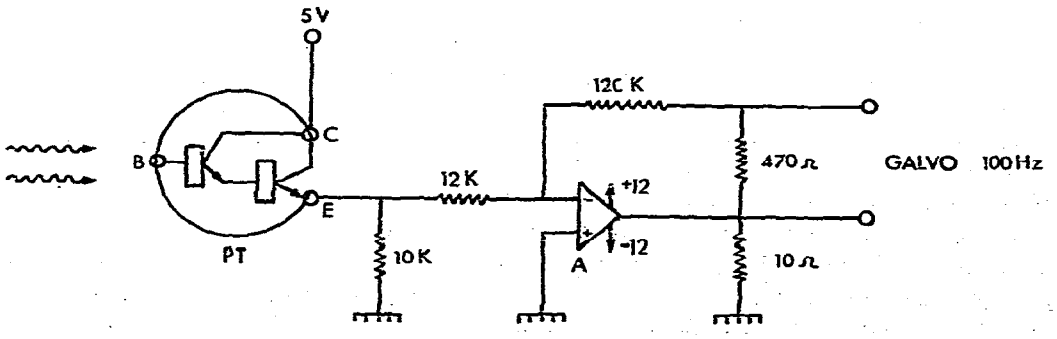

Fig. 3. Temperature measurement circuit.

The temperature measured in this way is obtained by calibrating the trap using a micro-thermocouple. The voltage across the trap is followed on another channel of the recorder, as shown in Fig. 2.

RESULTS

A typical run is shown in Fig. 4. The upper recording refers to the applied voltage and the lower to the measured temperature of the trap. It is evident that the trap is heated to about 400° within 20 msec and is thereafter held at about 350°.

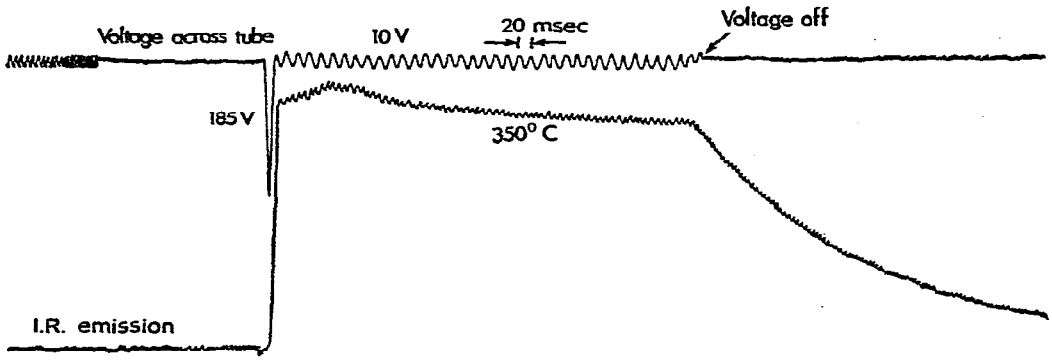

Fig. 4. Performance of heater.

The initial decrease in temperature can be ascribed to the attainment of thermal equilibrium of the trap with the environment.

By using a more powerful transformer, heating times of less than 20 msec should be possible.

REFERENCES

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