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APPLICATION OF A THERMAL CONDUCTIVITY DETECTOR WITH CONSTANT FILAMENT TEMPERATURE TO GAS CHROMATOGRAPHY WITH A HEAVY CARRIER GAS

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SUMMARY

An equation is suggested that gives an approximate relationship between (a) the temperature difference between the thermostat and the cell filament and (b) the power supplied and the nature of the carrier gas. It is shown that a catharometer in a conventional circuit cannot operate with heavy carrier gases that have low thermal conductivity. Three circuits for constant-filament-temperature catharometers are described; tests have shown that these circuits permit successful chromatographic separations of mixtures when gases of low thermal conductivity are used.

The advantages of thermal conductivity detectors are well known[1,2]. With increasing application of the vapours of various (mostly organic) solvents, catharometers have attracted more and more attention, because the most widely used high-sensitivity detectors are flame ionization cells that cannot operate with organic carrier vapours.

Thermal energy is transferred from the filament to the cell wall mostly by thermal conductivity[3], so that the filament temperature in the coaxial channel must be described by the following equation:

$$\Delta t = \frac{\sqrt{\lambda_2^2 + BN\sigma}}{\sigma} - \frac{\lambda_2}{\sigma} \tag{1}$$

where

Δt = temperature difference between the filament and the cell wall (°C);

λ_2 = thermal conductivity of the carrier gas at the cell wall temperature (W/m·°C);

N = electric power dissipated by the filament (W);

σ = thermal conductivity temperature coefficient of the carrier gas (W/m·°C^2)

B = geometry constant (m^{-1}).

This equation has been used to calculate the temperature of catharometer filaments in various carrier gases at various thermostat temperatures. The reliability of the calculation was checked by measurements of cell filament temperatures, preceded by calibration of the wires at various temperatures in the range 20–300° inside the thermostat. A small electric current, producing no appreciable heating of the filaments, was fed through the cells. The contact potential difference was eliminated by means of direct and reversed connections of the filament to the circuit (see Fig. 1). In order to eliminate the possibility of subjective errors, the filaments were disconnected from the circuit after measurements had been recorded and were then replaced with a resistance box, the resistance of which was adjusted until the instrument readings were identical in both instances. The resistance of the wire was plotted as a function of temperature; the relationship was linear within the temperature range used.

Various carrier gases were passed through the cell chambers at various temperatures in the thermostat while the operating current, varied from zero to the maximum possible value, was fed through the detector filaments (see Fig. 2). The filament temperature was determined via the filament resistance, *i.e.*, from measured values of the filament current and potential difference.

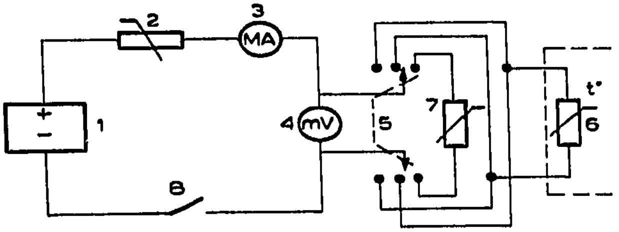


Fig. 1. Circuit for measuring cell filament resistance. 1 = Supply source; 2 = ballast rheostat; 3 = microammeter; 4 = millivoltmeter; 5 = switch; 6 = cell filament; 7 = resistance box; 8 = circuit breaker.

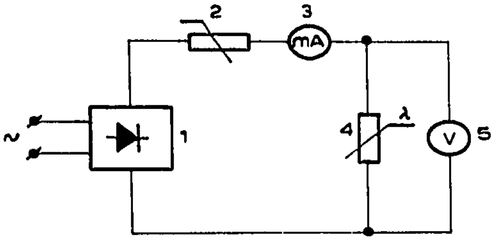


Fig. 2. Circuit for measuring cell filament temperature. 1 = Supply source; 2 = ballast rheostat; 3 = milliammeter; 4 = cell filament; 5 = voltmeter.

Fig. 3 shows calculated (broken lines) and measured (solid lines) values of the temperature difference as a function of the power dissipated by the filament in hydrogen as carrier gas. Fig. 4 shows similar curves in nitrogen as carrier gas; similar relationship were found for helium, argon and carbon dioxide. The curves may have different shapes depending on the relationship between the thermal conductivity, λ, and the thermal conductivity coefficient, σ, but the discrepancy between the calculated and observed temperatures does not exceed 10–15°.

The calculations, experimental results and operational experience explain why catharometers in modern chromatographs are used mostly with light carrier gases (hydrogen and helium). The application of catharometers with heavy carrier gases (*e.g.*, nitrogen, argon and carbon dioxide) is limited: standard detector circuits lead to excessive overheating of the filament owing to the low thermal conductivity of the carrier gas (see Table I), even with a low power supply to the filament and hence at low detector sensitivity.

Two conflicting requirements need to be satisfied when a thermal conductivity

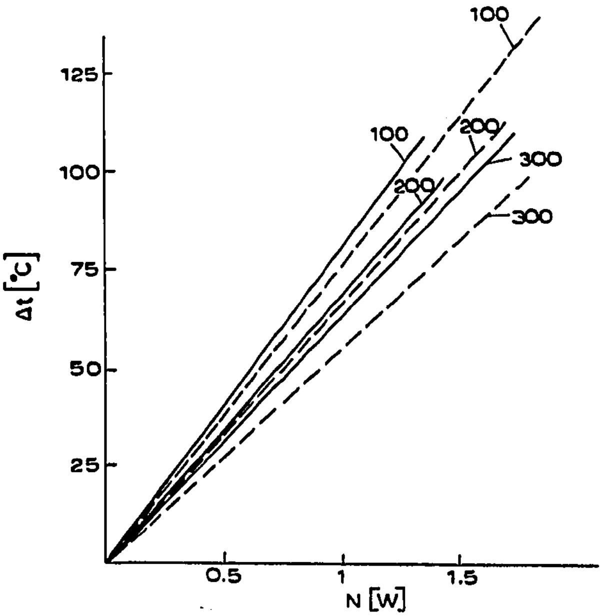


Fig. 3. Cell filament temperature as a function of power supply. Carrier gas, hydrogen. ——— Experimental results; – – –, calculated results.

cell is used in a conventional detector circuit with carriers of low thermal conductivity. On the one hand, the filament current must be increased so as to ensure sufficient detector response, but on the other hand this current must be reduced so as to prevent degradation of the filament and conversions of the separated sample components at increased temperatures, even at high concentrations of the sample in the chromatographic zone (especially in preparative chromatography).

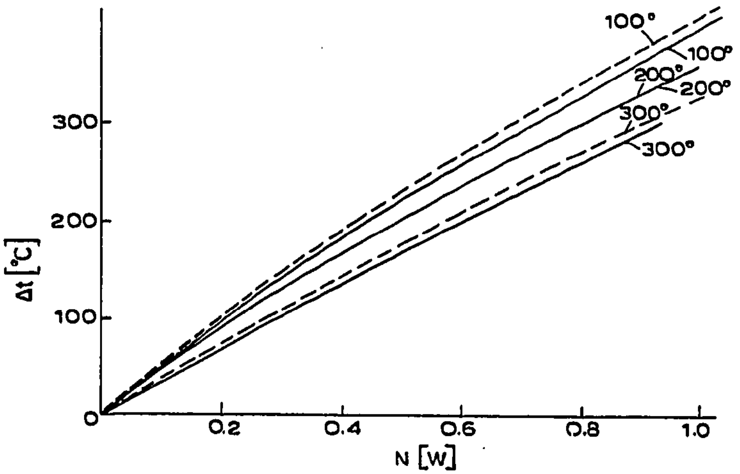


Fig. 4. Filament temperature as a function of power supply. Carrier gas, nitrogen. ———, Experimental results; – – –, calculated results. Calculated and experimental curves coincide up to 200° in the thermostat.

TABLE I

THERMAL CONDUCTIVITY (λ) OF GASES AND VAPOURS AT 120°

Compound	*10^4 λ (kcal/m·h·°C)*	*Compound*	*10^4 λ (kcal/m·h·°C)*
Hydrogen	1960	Carbon dioxide	215
Helium	1570	*n*-Hexane	196
Methane	414	Argon	190
Nitrogen	280	*n*-Heptane	180
Water	220	*n*-Octane	165
n-Pentane	213	Acetone	165

In order to solve this problem, we suggest below several arrangements in which catharometers are used. The principle of these circuits is a comparison of the electric resistance of the cell filament to the resistance of the reference resistor. The filament resistance (*i.e.*, its temperature) remains constant during the operation of these circuits.

The first circuit (Fig. 5) utilizes a single-chamber cell[4]. The filament is used as one arm (R_4) of a bridge in which two other arms, R_1 and R_2, are fixed resistors and a resistor box R_3 serves as the reference arm. The bridge circuit is connected to the supply source (SS) through the rheostat R_p and the variable ballast resistor R_B. Except for the arm R_4, all resistances in the bridge are independent of current. A reversible motor (M) is connected to the output of the amplifier (Am) placed in the measuring diagonal of the bridge. The motor moves the rheostat slide, and also the pen and indicating pointer of the recorder. The resistor R_3 is adjusted to a value identical with that of the cell filament R_4 at the temperature at which this filament is to operate. The resistor R_B is set at its maximum value, the amplifier supply is turned on and, after the warm-up period of the amplifier electron tubes, the main supply source (SS) is switched on; the pointer of the recorder moves to the edge of the scale because, at small currents, R_3 is greater than the detector resistance R_4. The current through the bridge, including that through the filament R_4, is then increased by reducing the resistance of the resistor R_B, so that the temperature of the cell filament increases and the resistance of the filament increases; when it becomes equal to R_3,

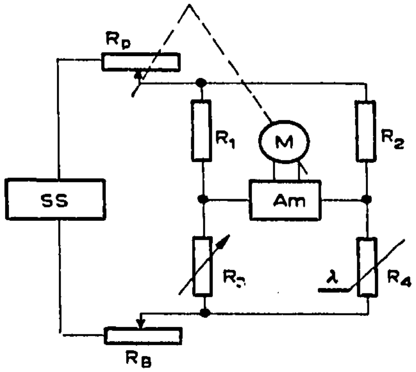


Fig. 5. Single-chamber detector circuit with current control.

the bridge becomes equilibrated and the pointer of the recorder takes a definite position on the scale. Small deviations from equilibrium are amplified and actuate the electric motor (M), which shifts the slide of the rheostat R_p until these deviations are compensated. If the thermostat temperature and gas flow-rate are kept constant, the balanced state of the bridge may be perturbed by changes in the thermal conductivity of the carrier gas, *i.e.*, when a concentration zone passes through the detector. Thus, the movement of the pointer on the scale records the chromatographic peaks. It is obvious that unless the pointer reaches the stopper and if compensation is effective, the temperature of the filament remains constant.

The sensitivity of this circuit is given by the equation

$$\frac{\mathrm{d}R_p}{\mathrm{d}\lambda} = U_n \sqrt{\frac{K_1 R_4}{\Delta t \lambda^3}} \tag{2}$$

where

U_n = supply voltage;
K_1 = proportionality coefficient;
R_4 = resistance of the cell filament (arm R_4) (ohms); and
R_p = resistance of the rheostat R_p (ohms).

Eqn. 2 shows that the cell response in this circuit increases when carrier gases of low thermal conductivity are used. The detector response in this circuit can, in principle, be varied over a wide range by increasing the supply voltage U_n and the

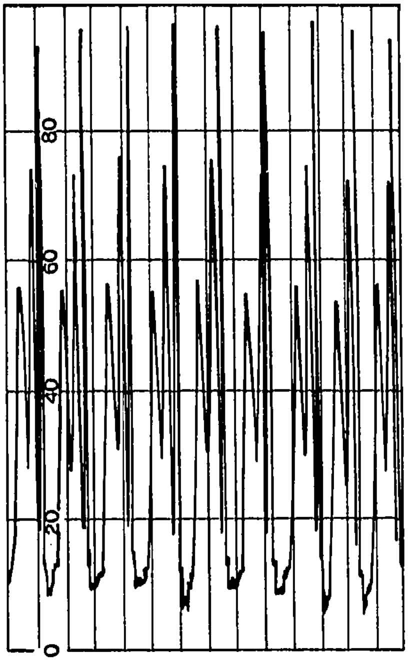
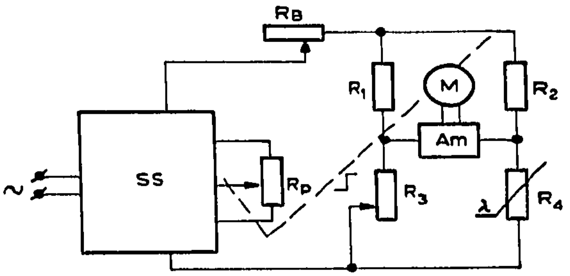


Fig. 6. Chromatogram of separation of a model hydrocarbon mixture of *n*-heptane, *n*-decane and *n*-dodecane.



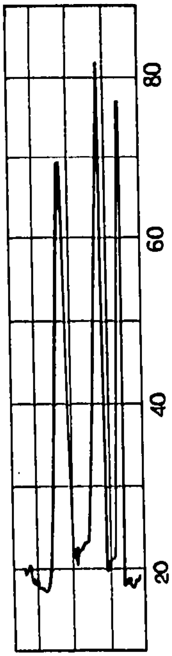


Fig. 7. Single-chamber detector circuit with voltage control.

Fig. 8. Chromatogram of separation of a mixture of sulphur-containing compounds (diethyl sulphide, ethyl *n*-propyl sulphide, di-*n*-propyl sulphide).

ballast resistance R_B and by reducing the temperature difference Δt. However, in practice, this response is limited owing to the stringent constraints on the supply source and the amplifier sensitivity. Nonetheless, the first use of the described circuit using nitrogen as the carrier gas resulted in a four-fold increase in the response.

A similar circuit, involving electronic instead of electromechanical compensation, has been described by Wittebrood[5].

Fig. 6 shows a chromatogram for the separation of an artificial mixture of fractions of *n*-heptane, *n*-decane and *n*-dodecane at a thermostat temperature of 180° in a 2.6 m × 26 mm I.D. column filled with Spherochrome coated with 10% neopentyl glycol succinate. Carbon dioxide was used as the carrier gas at a flow-rate through the column of 1 l/min and through the detector of 60 ml/min. The supply voltage was 300 V and the value of the reference resistance R_3 was 72 ohms, which corresponds to 260° (the temperature difference in relation to the cell walls was $\Delta t = 80°$). The chromatograph was operated in the preparative automatically recycling mode.

The circuit was also tested with water vapour as the carrier gas. The second circuit differs from the one above in that the control rheostat R_p is not connected in series with the supply source but makes part of the supply circuit (Fig. 7). When a concentration zone passes through the cell, the bridge equilibrium is disturbed owing to a change in thermal conductivity and the motor M shifts the slide of the rheostat R_p. This slide displacement causes a change in the output voltage U_{out} fed to the

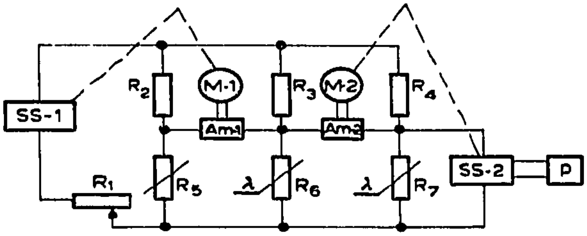


Fig. 9. Electrical circuit of the two-chamber thermal conductivity detector with constant filament temperature.

measurement bridge and hence also a change in the power supply to the cell filament.

The response of this circuit is given by the equation

$$\frac{\mathrm{d}\,U_{\mathrm{out}}}{\mathrm{d}\,\lambda} = K_2\,(R_B + R_4)\sqrt{\frac{\Delta t}{R_4\,\lambda}} \qquad (3)$$

where

U_{out} = output voltage of the rectifier;
K_2 = proportionality coefficient; and
R_B = ballast rheostat resistance (ohms).

The detector response in this circuit increases as the temperature difference Δt increases and as the thermal conductivity of the carrier gas λ decreases.

This circuit permitted a preparative separation of a mixture of technical xylenes to be achieved. Fig. 8 shows the chromatogram of a preparative separation of a mixture resulting from a synthesis of sulphides and consisting of diethyl sulphide, ethyl *n*-propyl sulphide and di-*n*-propyl sulphide; *n*-pentane was used as the carrier gas.

The third circuit (Fig. 9) operates with two- or four-chamber cells, *i.e.*, with any standard catharometer, and requires no changes in the gas circuit.

The supply source SS-1 feeds the double bridge through the ballast resistor R_1. Resistors R_2, R_3 and R_4 have identical resistances, R_5 is the reference resistor determining the temperature of the cell filament, R_6 is the filament in the detector reference cell and R_7 is the filament in the working chamber. The out-of-balance voltage in the left half of the bridge is amplified by the amplifier Am-1 and controls the output voltage of the supply unit SS-1 by means of the motor M-1, compensating variations of the cell regime. The out-of-balance signal in the right half of the bridge is due to the chromatographic zone passing through the working chamber of the detector. This out-of-balance signal is amplified by the second amplifier Am-2, and a compensating voltage U_k is generated on the supply source (SS-2) by means of the motor M-2. This compensating voltage is measured and recorded by the potentiometer P as the chromatographic peak.

Fig. 10 shows a chromatogram recorded in the automatic preparative separation of the three-component model mixture with carbon dioxide as carrier gas. A conventional catharometer was used in a PAHV-05 chromatograph with a specially constructed measuring bridge.

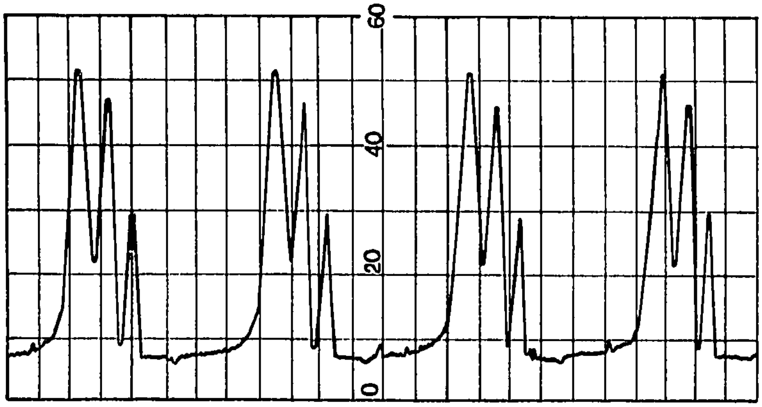


Fig. 10. Chromatogram of separation of a hydrocarbon mixture (*n*-heptane, *n*-nonane, *n*-decane).

The circuits described above permit the use of chromatographs, including also preparative models, for separating mixtures of compounds when heavy gases and vapours are used as carrier gases.

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