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Journal of Chromatography A, 715 (1995) 287–297

JOURNAL OF CHROMATOGRAPHY A

Assessment of some possibilities for improving the performance of gas chromatographic thermal conductivity detectors with hot-wire sensitive elements

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First received 16 March 1994; revised manuscript received 18 April 1995; accepted 19 May 1995

Abstract

The possibilities for improving the performance of gas chromatographic thermal conductivity detectors (TCD) by using hot-wire sensitive elements with appropriate design and increased resistance were studied. It is shown that the design of the traditional TCD with one-way heat conduction, and also the new kind of sensitive element design with two-way heat conduction, in which one of the filament leads is assembled inside the coil along its axis, can be optimized. The best TCD performance can be achieved if the sensitive element spiral pitch is minimal and the spiral radius is equal to r_c/e in the case of one-way heat conduction and to the mean radius $(r_c + r_l)/2$ in the case of two-way heat conduction, where r_c and r_l are the radiuses of the gas cavity and of the central filament lead, and $e \approx 2.7$ is the Napierian number. Further, the optimization of the sensitive element design provides an increase in its resistance, which additionally improves the TCD performance. Following this approach and taking into account the ultimate capabilities of modern electronics, two new optimized designs of the sensitive elements with about 650 Ω resistance at 0°C, that after the numerical estimations presented could improve the TCD performance more than tenfold, are developed and proposed for further experimental studies.

1. Introduction

The principle of operation and the factors affecting thermal conductivity detector (TCD) output signals have been treated in many publications and are summarized in several books [1,2]. It has been shown that the performance of the TCD with four hot-wire sensitive elements can be improved if the Wheatstone bridge is supplied from a d.c. source with constant-current control [3] (Fig. 1) and if the filament resistance at 0°C, R_0, is increased to 100 Ω [4,5]. The latter limitation is due to the traditional design of the sensitive elements and of the d.c. sources currently used in commercial gas chromatographs. Since the restrictions concerning the d.c. sources are not crucial for modern electronics, the problem of designing hot-wire sensitive elements with $R_0 = 500–700$ Ω becomes important. The theoretical and some practical aspects of this problem are treated in this paper. The dependence of TCD operation on the design and the resistance

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0021-9673/95/$09.50
SSDI 0021-9673(95)00595-1

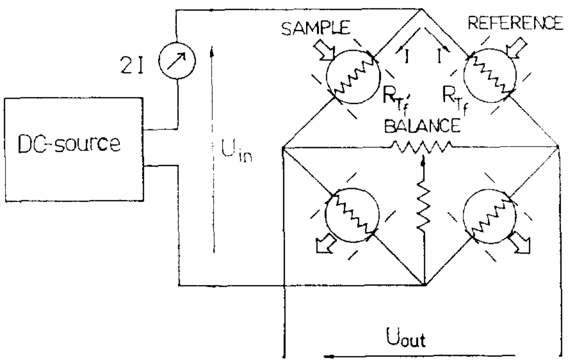

Fig. 1. TCD with four hot-wire sensitive elements in a Wheatstone bridge supplied from a d.c. source with constant current control.

of its sensitive elements was studied with the intention of developing and proposing new types of high-resistance hot-wire sensitive elements that could substantially improve the TCD performance.

2. Theoretical

The output signal of the TCD shown in Fig. 1 is due to the difference between the temperatures T'_f and T_f (°C) of the filaments in the TCD sample and reference cavities due to the sample components entering the detector as a mixture with the carrier gas. Taking into account the temperature dependence $R_{Tf} = R_0(1 + \alpha T_f)$ of the filament resistance, the TCD output signal is

$$U_{out} = I(R_{Tf'} - R_{Tf}) = IR_0\alpha(T'_f - T_f) \quad (1)$$

where I (A) is the current heating the sensitive elements, $R_0 = \rho_0 l_f / S_f$ (Ω) is the resistance of the filaments at 0°C and α (°C^{-1}) is the coefficient of resistance of the material with resistivity ρ_0 (Ω cm), from which the filaments with length l_f (cm) and cross-section $S_f = \pi r_f^2$ (cm^2) are made.

While the temperature T_c (°C) of the TCD block is kept constant, the filament temperature is determined from the heat balance established between the filament heat flux and the heat losses through the thermal conductivity and the heat capacity of the gas mixture in the cavity considered, the heat conduction in the hot wire support, the convection and the radiation.

If the sum of the last three types of heat losses is denoted by S, then the heat balance in the TCD reference cavity is

$$I^2R_0(1 + \alpha T_f)/J = G\lambda(T_f - T_c) + V_\mu C_p(T_g - T_c) + S \quad (2)$$

where $J = 4.19$ J/cal is the Joule equivalent, G (cm) is the TCD cell factor, λ (cal/cm · s · °C) is the thermal conductivity of the carrier gas, V_μ = 273 V_{vol}/22420 (273 + T_m) (mol/s) is the molar flow-rate of the gas through the cavity, calculated from the volume flow-rate V_{vol} (ml/s) and the temperature T_m (°C) of the measuring device, C_p (cal/mol · °C) is the molar heat capacity of the carrier gas at constant pressure and T_g (°C) is the average temperature of the gas leaving the TCD reference cavity.

Since the calculation of G and T_g, needed for solving the TCD main Eq. 2, requires information about the sensitive element design and the temperature distribution in the gas cavity, some supplementary assumptions are made. The common features of the considered sensitive element designs are that the filament is coiled in a spiral of length l_s, coaxially situated in the TCD gas cavity (Fig. 2), and that the radius of

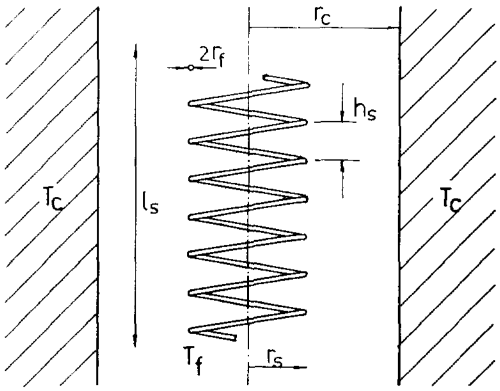

Fig. 2. TCD temperatures and sensitive element design parameters.

the spiral r_s exceeds its pitch h_s, ensuring practically acceptable values of l_s even if the high-resistance filament is up to 1 m long. The supplementary assumption about the temperature distribution in the gas cavity is that all the points of the cylindrical surface formed by the coil are at the same temperature T_f, if the spiral pitch h_s is small enough in comparison with the radiuses of the sensitive element r_s and of the TCD gas cavity r_c. Then the temperature distribution between the coil and the wall of the cavity is

$$T_{out}(r) = \frac{T_f \ln(r_c/r) + T_c \ln(r/r_s)}{\ln(r_c/r_s)}, \quad r_s \leq r \leq r_c \tag{3}$$

and if the region inside the coil is filled with gas only, its temperature at the above assumption has to be T_f, as shown in Fig. 3a.

In this case with one-way heat conduction (outwards to the cavity wall), the TCD cell factor is $G_1 = 2\pi l_s/\ln(r_c/r_s)$, the average temperature of the gas departing the TCD reference cavity is

$$T_g = \frac{1}{r_c^2}\left[\int_0^{r_s} T_f \, d(r^2) + \int_{r_s}^{r_c} T_{out}(r) \, d(r^2)\right] = T_c + \frac{T_f - T_c}{2r_c^2} \cdot \frac{r_c^2 - r_s^2}{\ln(r_c/r_s)}$$

and the filament temperature T_f derived from the TCD main Eq. 2 is

$$T_f = T_c + \frac{I^2R_0(1+\alpha T_c)/J - S}{G_1\lambda + V_\mu C_p(r_c^2 - r_s^2)/2r_c^2 \ln(r_c/r_s) - \alpha I^2 R_0/J} \tag{4}$$

In view of the fact that the heat losses denoted by S are virtually independent of the gas composition and their percentage in the total sum of losses is relatively small, in the following analysis the term S is ignored and Eq. 4 is transformed into

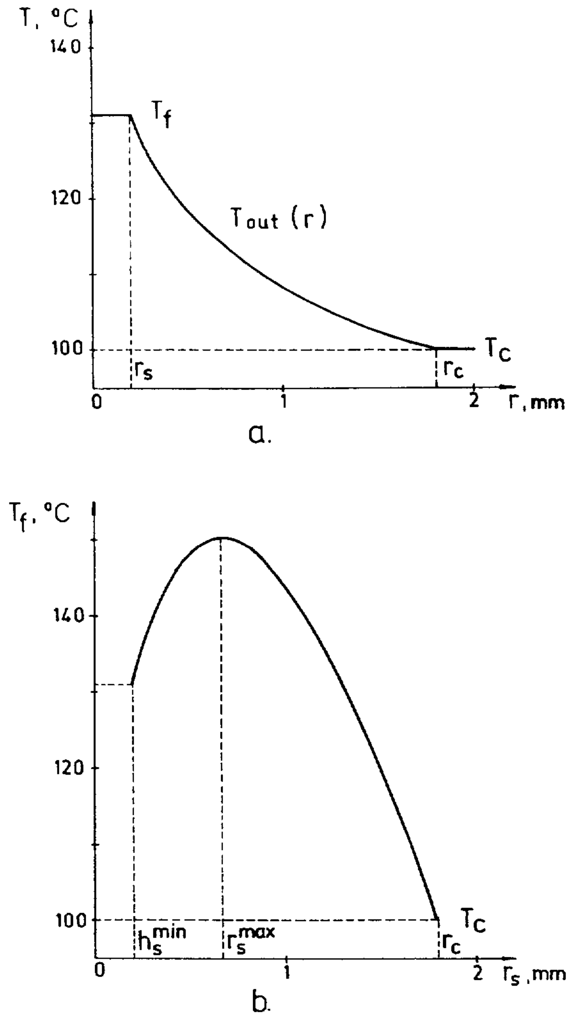

Fig. 3. TCD with one-way heat conduction: (a) temperature distribution; (b) filament temperature. Conditions assumed in the numerical calculations: carrier gas, helium at a flow-rate of 60 ml/min measured at 20°C; tungsten filaments of $r_f = 5.7$ μm coiled in spirals with r_s (mm), $R_0 = 300$ r_s (Ω), $h_s = 200$ μm and $l_s = 18$ mm; heating current $I = 50$ mA corresponding to $x_{max} = 5$ mol-% for the design version 2 in Fig. 5.

$$T_f = T_c + (1/\alpha + T_c)\frac{A}{1 + BC_p - A} \tag{5}$$

using for simplifying the equations the symbols A and B instead of the expressions $\alpha I^2 R_0/JG_1\lambda$ and $V_\mu(r_c^2 - r_s^2)/4\pi l_s \lambda r_c^2$, respectively.

The TCD output signal, derived from Eq. 1 using Eq. 5, is

$$U_{out} = IR_0(1+\alpha T_c)\frac{A}{1+BC_p-A} \cdot \frac{1-\lambda'/\lambda + B(C_p - C_p')}{\lambda'/\lambda + BC_p' - A} \quad (6)$$

where λ' and C_p' refer to the gas mixture in the sample cavities.

The last term of Eq. 6 can be expressed as a function $f(x)$ of the molar concentration x of the sample component i entering the TCD as a mixture with the carrier gas, using the well known relationship $1/\lambda' = 1/\lambda + (1/\lambda_i - 1/\lambda)x$, which is valid at component concentrations $x \leq 10$ mol-%, the assumption $C_p' = C_p + (C_{p,i} - C_p)x$ and the symbols $L = \lambda/\lambda_i - 1$, $M = A - BC_p$ and $N = B(C_{p,i} - C_p)$ for simplifying the equations. Then,

$$f(x) = \frac{(L-N)x - LNx^2}{(1-M) - (LM-N)x + LNx^2} \quad (7)$$

and since $L >> N$ owing to the great thermal conductivity of the carrier gases commonly used, the TCD response is positive. Regardless of the non-linearity of $f(x)$, Eq. 7, if the component concentrations are small enough, then the TCD operation can be assumed to be linear with a coefficient of sensitivity

$$K = \left.\frac{dU_{out}}{dx}\right|_{x=0} = IR_0(1+\alpha T_c)\frac{(L-N)A}{(1-M)^2} \quad (8)$$

which in the traditional analysis of the TCD performance is the main subject of theoretical estimations, whereas the detection level and even the TCD linear range are determined experimentally. However, the knowledge of U_{out} provides a wider estimation of TCD performance including not only T_f and K, but also the upper limit x_{max} (mol-%) of the TCD linear range, the corresponding maximum output signal $U_{max} = Kx_{max}$ and the d.c. source voltage $U_{in} = 2IR_0(1 + \alpha T_f)$ (V) and the power $P = 2IU_{in}$(W) required for supplying the Wheatstone bridge with the necessary constant current.

Since x_{max} is defined by

$$\left|\frac{U_{out} - Kx}{Kx}\right| = \delta$$

if the deviations from the linearity are restricted to $\delta = 3\%$, then using Eqs. 6, 7 and 8 the actual equation for calculating the upper limit of the TCD linear range is

$$\left|\frac{\left(\frac{L-N}{1-M} - \frac{L^2}{L-N}\right)x - \frac{LN}{1-M}\cdot x^2}{1 - \left(\frac{L-N}{1-M} - L\right)x + \frac{LN}{1-M}\cdot x^2}\right| = 0.03 \quad (9)$$

3. Results and discussion

The results presented below can be explained more consistently if the small terms involving the heat capacities in the relationships used for the TCD performance estimation are discarded, giving

$$\Delta T = T_f - T_c \approx (1/\alpha + T_c)\frac{A}{1-A}$$

$$K \approx L(1+\alpha T_c)R_0 \cdot \frac{AI}{(1-A)^2}$$

$$x_{max} \approx \frac{2.9}{L}\cdot\frac{1-A}{A}$$

$$U_{max} \approx 0.029(1+\alpha T_c)R_0 \cdot \frac{I}{1-A}$$

$$U_{in} \approx 2(1+\alpha T_c)R_0 \cdot \frac{I}{1-A} \approx 69\ U_{max}$$

$$P \approx 4(1+\alpha T_c)R_0 \cdot \frac{I^2}{1-A} \approx 137\ IU_{max} \quad (10)$$

Taking into account the form of the expression A introduced above, the relationships (10) show that:

(a) the main factor affecting the TCD performance is the filament heating current I, but only the increase in TCD block temperature T_c improves the performance parameters ΔT, K and U_{max} without a degradation of the upper limit x_{max} of the TCD linear range;

(b) the temperature difference ΔT is inversely proportional to x_{max} with a coefficient that depends on L, α and T_c only;

(c) the improvement of the maximum output signal U_{max} generated in the TCD linear range requires a proportional increase of the d.c. source voltage V_{in} and power P (which is proportional to I again);

(d) the increase in the filament resistance R_0 is a favourable factor for improving the TCD performance, but its clarification needs a further analysis of the expression A, which comprises all the others sensitive element design parameters.

The detailed study of the expression A reveals that it is not influenced by the value of the filament resistance R_0 taken alone, but by the dimensions of the sensitive element, for some of which an optimum proportion exists. These conclusions follow from the known relationship $l_f = l_s[(2\pi r_s/h_s)^2 + 1]^{1/2}$, which for $r_s \geqslant h_s$ can be approximated as $l_f = 2\pi l_s r_s/h_s$. Then, concerning sensitive elements coiled from filaments of a given material and cross-section, the correct form of the expression A is

$$A = \frac{\alpha I^2 \rho_0}{J\lambda S_f} \cdot \frac{r_s}{h_s} \ln(r_c/r_s) \quad (11)$$

The possibilities of increasing A by varying r_s and h_s depend on the supplementary requirements imposed. When both the detector volume $V_d = \pi r_c^2 l_s$ and R_0 are predetermined, then the r_s/h_s ratio is also predefined, but the value of A can be increased by minimizing to the practically acceptable limits both r_s and h_s in the same proportion. For example, consider a "classical" TCD with $r_c = 1.8$ mm and $V_d \approx 200$ μl, whose sensitive elements are coiled from tungsten filaments of $r_f = 5.7$ μm in spirals with $R_0 = 60$ Ω, $l_s = 18$ mm and $r_s = h_s = 400$ μm. This TCD is used in the present work for comparison purposes regardless of the fact that most of the sensitive elements currently available have lower performance because their spirals are not coaxially placed in the TCD gas cavitites and are of lower resistance. However, the performance assessments ΔT and K of the considered "classical" TCD can be improved with more than 50% by increasing $\ln(1800/200)/\ln(1800/400) = 1.46$ times the value of A in Eq. 11 through a decrease in both r_s and h_s to 200 μm, while keeping all the other design parameters and operational conditions unchanged.

When only the detector volume V_d is predetermined, but the filament resistance R_0 is allowed to vary, the sensitive element spiral radius r_s and pitch h_s are independent. Since the expression A depends inversely on h_s, it can be increased by reducing h_s to the practically acceptable limit. Then, by means of the spiral radius the value of A can be increased still further and even maximized, since Eq. 11 as a function of $r_s \in [h_s^{min}, r_c]$ has a maximum at $r_s^{max} = r_c/e$, where $e \approx 2.7$ is the Napierian number. In view of the fact that the existence of such a maximum is essential for TCD design optimization and performance improvement, the direct influence of r_s on the filament temperature T_f according to Eq. 5 is quantitatively evaluated. The supposed common TCD operational conditions and the design parameters used are explained in Fig. 3, where the increase in R_0 proportionally to r_s is also described. The relationship presented in Fig. 3b shows that since the "heat capacity effect" involved in Eq. 5 by the term BC_p is almost negligible, the filament temperature T_f as a function of r_s follows the course of the expression A and has a marked maximum at a sensitive element spiral radius very close to r_s^{max}. Further, it is important to note that in addition to a maximum value of the expression A, the optimization of the sensitive element design by using h_s^{min} and r_s^{max} provides a higher resistance R_0 than of the "classical" TCD, because r_s^{max} as a $1/e$ part of the gas cavity radius is relatively large. Therefore, the optimization of sensitive element design is an important approach for TCD performance improvement, because in accordance with Eq. 10 such sensitive elements not only have high values of ΔT (and lower values of x_{max}, which is inversely proportional to ΔT), but also, owing to the increased R_0, they have additionally improved coefficients of sensitivity K and higher values of the maximum output signals U_{max} generated in the TCD linear range.

The next possibility for TCD performance improvement involves a new kind of sensitive element design, based on the fact that if the spiral radius r_s is large enough, one of the filament leads with temperature T_c can be assembled inside the coil along its axis. Then the temperature distribution between the spiral and the cavity wall is $T_{out}(r)$ from Eq. 3, but between the central lead with radius r_l and the coil the temperature distribution is

$$T_{in}(r) = \frac{T_f \ln(r/r_l) + T_c \ln(r_s/r)}{\ln(r_s/r_l)}, \quad r_l \leq r \leq r_s$$

as it is shown in Fig. 4a.

In this case of two-way heat conduction (outwards to the cavity wall and inwards to the central lead), the TCD cell factor is $G_2 = 2\pi l_s \ln(r_c/r_l)/\ln(r_c/r_s)\ln(r_s/r_l)$, the average temperature of the gas leaving the TCD reference cavity is

$$T_g = \frac{1}{r_c^2 - r_l^2}\left[\int_{r_l}^{r_s} T_{in}(r)\,d(r^2) + \int_{r_s}^{r_c} T_{out}(r)\,d(r^2)\right]$$
$$= T_c + \frac{T_f - T_c}{2(r_c^2 - r_l^2)}\left[\frac{r_c^2 - r_s^2}{\ln(r_c/r_s)} - \frac{r_s^2 - r_l^2}{\ln(r_s/r_l)}\right]$$

and the filament temperature is represented by Eq. 5 with $A = \alpha I^2 R_0 / J G_2 \lambda$ and

$$B = \frac{V_\mu}{4\pi l_s \lambda}\left[\frac{r_c^2 - r_s^2}{r_s^2 - r_l^2} - \frac{\ln(r_c/r_s)}{\ln(r_c/r_l)}\right]$$

The possibilities for TCD performance improvement by means of the new kind of sensitive element design are studied using the correct form of the expression A for the case of two-way heat conduction:

$$A = \frac{\alpha I^2 \rho_0}{J \lambda S_f} \cdot \frac{r_s}{h_s} \cdot \frac{\ln(r_s/r_l)\ln(r_c/r_s)}{\ln(r_c/r_l)} \tag{12}$$

and following the same approach as above in the last case of one-way heat conduction. The results obtained are similar to the aforesaid also, because in Eq. 12 A as a function of $r_s \in [r_l, r_c]$ has a maximum at $r_s^{max} = (r_l r_c)^{1/2} \exp\{[\ln^2(r_c/r_l)/4 + 1]^{1/2} - 1\}$ and the filament temperature T_f evaluated quantitatively as a function of r_s according to Eq. 5 has a marked maximum at a spiral radius very close to r_s^{max}, as is shown in Fig. 4b. Further, owing to the almost doubled heat flux in the new kind of sensitive elements, the maximum values of the expression A and the filament temperature T_f are lower than in the TCD with one-way heat conduction and optimized design, whereas in the considered domain of r_l and r_c the optimum value r_s^{max} for the case of two-way heat conduction can be approximated with the mean radius $(r_l + r_c)/2$ and is greater than r_c/e. Therefore, the optimization of the new kind of sensitive element design by using h_s^{min} and r_s^{max} in addition to a sufficiently high value of the expression A in Eq. 12 provides a significant increase in filament resistance R_0 with

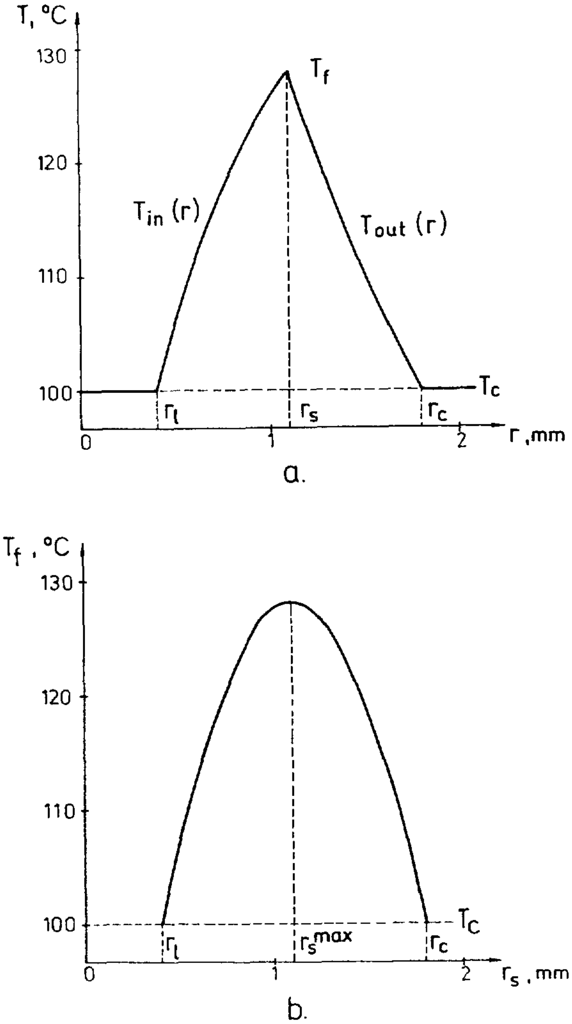

Fig. 4. TCD with two-way heat conduction: (a) temperature distribution; (b) filament temperature. Conditions assumed in the numerical calculations: carrier gas, filament and spirals as in Fig. 3; heating current $I = 52$ mA corresponding to $x_{max} = 5$ mol-% for the design version 4 in Fig. 5.

a corresponding improvement of the TCD coefficient of sensitivity K and of the maximum output signal U_{max} generated in the TCD linear range.

The performance assessments of the considered TCD are evaluated quantitatively designating x_{max} as an argument with a range from 1 to 10 mol-% and solving Eq. 9 for the quantity M introduced above. The solution is

$$M = \frac{3 + \left(2.03 + \frac{N}{L-N} + 0.0103Lx_{max}\right)Nx_{max}}{3 + \left(1.03 + \frac{N}{L-N}\right)Lx_{max}}$$

and through it the expression A, the filament heating current I necessary for the TCD operation in the $[0, x_{max}]$ linear range and T_f, K, U_{max}, U_{in} and P are evaluated according to the complete equations given above.

The numerical estimations thus obtained for the four sensitive element design versions discussed above under assumed common TCD operational conditions are presented in Fig. 5 in a traditional manner, using as an independent variable the constant current needed for supplying the Wheatstone bridge and ignoring as unimportant the assessments of the required d.c. source voltage and power. Since the relationships in Fig. 5 corroborate the possibility of TCD performance improvement by means of sensitive element design optimization and filament resistance increase, two new types of TCD hot-wire sensitive elements with $R_0 \approx 650\ \Omega$ and detector volumes $V_d \approx 200\ \mu m$ are evaluated and proposed for development and further experimental study.

The first new sensitive element is of optimized one-way heat conduction design and its resistance $R_0 = 640\ \Omega$ is achieved by increasing the

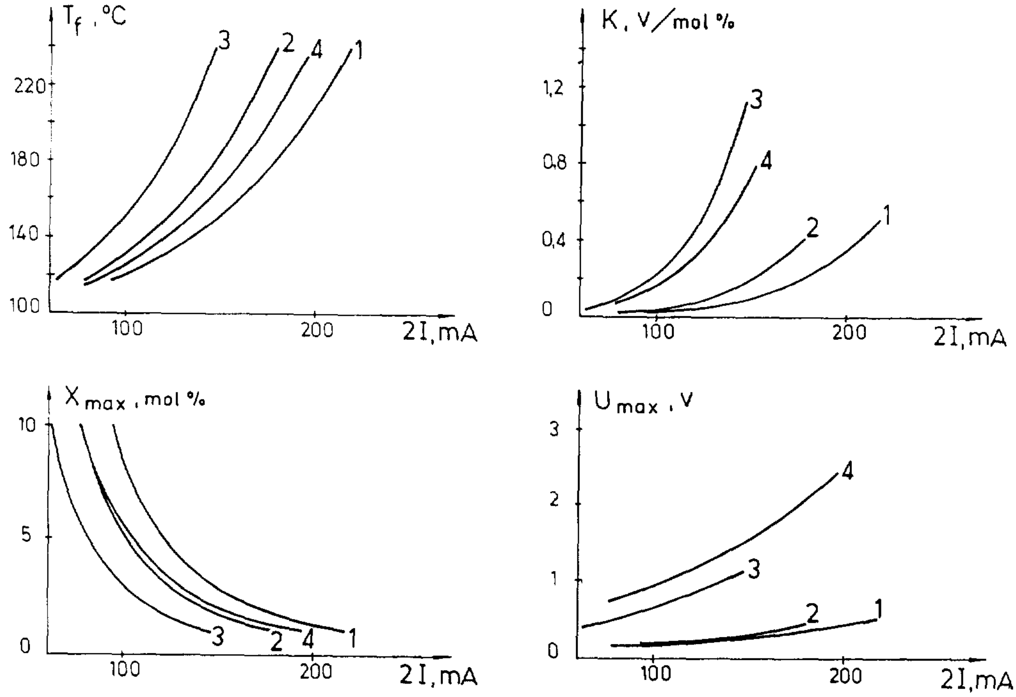

Fig. 5. TCD performance. Conditions assumed in the numerical calculations: TCD block temperature, 100°C; component, propane in the same carrier gas as in Fig. 3; filament as in Fig. 3 coiled in spirals with r_s or r_s^{max} for four sensitive element design versions with detector volume $V_d \approx 200\ \mu l$ ($r_i = 0$ represents the TCD with one-way heat conduction): (1) $r_c = 1.8$ mm, $r_i = 0$, $r_s = 400\ \mu m$, $R_0 = 60\ \Omega$, $h_s = 400\ \mu m$, $l_s = 18$ mm; (2) $r_c = 1.8$ mm, $r_i = 0$, $r_s = 200\ \mu m$, $R_0 = 60\ \Omega$, $h_s = 200\ \mu m$, $l_s = 18$ mm; (3) $r_c = 1.8$ mm, $r_i = 0$, $r_s^{max} = 660\ \mu m$, $R_0 = 200\ \Omega$, $h_s = 200\ \mu m$, $l_s = 18$ mm; (4) $r_c = 1.8$ mm, $r_i = 0.4$ mm, $r_s^{max} = 1100\ \mu m$, $R_0 = 330\ \Omega$, $h_s = 200\ \mu m$, $l_s = 18$ mm;

spiral length to $l_s = 190$ mm, while the detector volume $V_d = \pi r_c^2 l_s$ is kept restricted by reducing the gas cavity radius to $r_c = 0.54$ mm. Taking into account the known cell factor $G = 2\pi l_s / \ln(0.54a/r_s)$ of a gas cavity with square cross-section, the value of r_c corresponds to a square of side $a = 1$ mm.

The second new sensitive element is of optimized two-way heat conduction design and its resistance $R_0 = 660\ \Omega$ is achieved by decreasing the spiral pitch to the technologically accessible limit $h_s^{min} = 100\ \mu$m, while all the other parameters of the design version 4 in Fig. 5 are kept unchanged.

The quantitatively assessed complete TCD performance of the two new types of high resistance sensitive elements with optimized designs is presented in Fig. 6 in comparison with the "classical" TCD described above. The evaluated relationships suggest, that in accordance with Eq. 10, all sensitive element types operate in a given linear range at almost the same filament temperature (Fig. 6b) and the values of T_f are inversely proportional to x_{max}. Nevertheless, owing to their inherent high coefficients of sensitivity (Fig. 6c), which become higher with increase in TCD block temperature T_c in Eq. 8, the maximum output signals generated in the linear ranges of the new types of sensitive elements are 1–5 V (Fig. 6d) without involving additional amplifiers. The well known fact that the output signals generated by most of the TCDs currently used are below 0.1 V, and the ratios 0.477:0.274:0.045 and 2.384:1.371:0.226 between the values of K and U_{max} for the design versions 1, 2, and 3 in Fig. 6 at $x_{max} = 5$ mol-% allow the conclusion that the proposed high-resistance hot-wire sensitive elements with optimized designs could improve the TCD performance more than tenfold.

The comparison of the two new designs shows that the former allows a stronger heating current (Fig. 6a) owing to its minimal (equal to h_s) spiral radius and provides higher sensitivity and a greater output signal (Fig. 6c and d). However, its requirements for the d.c. source voltage and power necessary for supplying the TCD are severe (Fig. 6e and f) and with increase in TCD block temperature become rigorous ($U_{in} = 290$ V and $P = 40$ W for $x_{max} = 5$ mol-% at $T_c = 300$°C after a supplementary calculation), but still accessible for the ultimate capabilities of modern electronics.

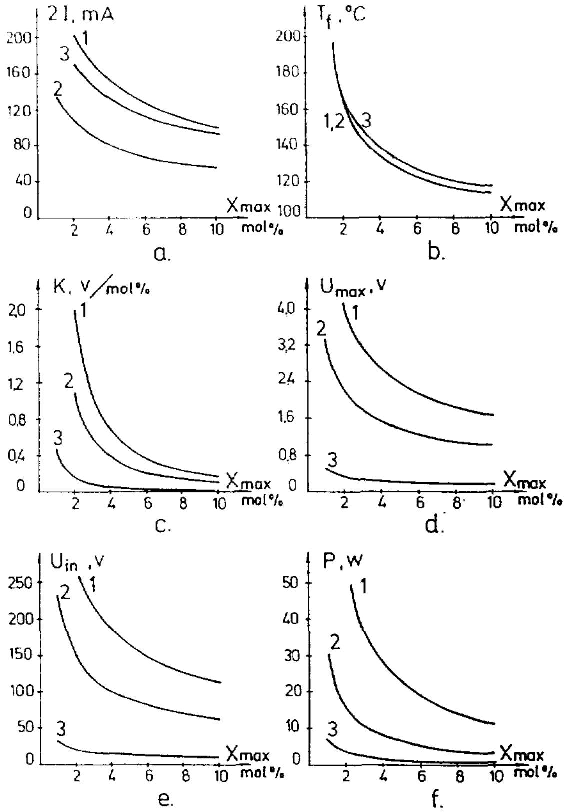

Fig. 6. TCD performance and d.c. source requirements. Two new high-resistance sensitive elements with optimized designs (1 and 2) in comparison with a "classical" TCD (3) the same as design version 1 in Fig. 5. Conditions assumed in the numerical estimations as in Fig. 5. (1) $r_c = 0.54$ mm, $r_1 = 0$, $r_s^{max} = 200\ \mu$m, $R_0 = 640\ \Omega$, $h_s = 200\ \mu$m, $l_s = 190$ mm; (2) $r_c = 1.8$ mm, $r_1 = 0.4$ mm $r_s^{max} = 1100\ \mu$m, $R_0 = 660\ \Omega$, $h_s = 100\ \mu$m, $l_s = 18$ mm; (3) $r_c = 1.8$ mm, $r_1 = 0$, $r_s = 400\ \mu$m $R_0 = 60\ \Omega$, $h_s = 400\ \mu$m, $l_s = 18$ mm.

The final results of this work is the development of two practical designs of high-resistance sensitive elements, which implement the best possibilities for TCD performance improvement obtained above for both cases of heat conduction.

In the first design developed, which corresponds to version 1 in Fig. 6 and is shown in Figs. 7 and 8, the coil 1 of length 190 mm is situated in the ten channels 2 with cross-section 1×1 mm^2 of the element body 3 and is bent between the adjacent channels through the helical grooves 5 on the insulating pegs 4. The body 3 is coupled in the element base 6 and is fastened by the nut 7, while the leads 8 of the coil are hermetically embedded in the perforations 9 by the insulators 10. The assembled sensitive elements are placed in the nests 11 of the TCD block 12, whose channels 13 split the gas flows among the relevant sensitive elements. Thus the

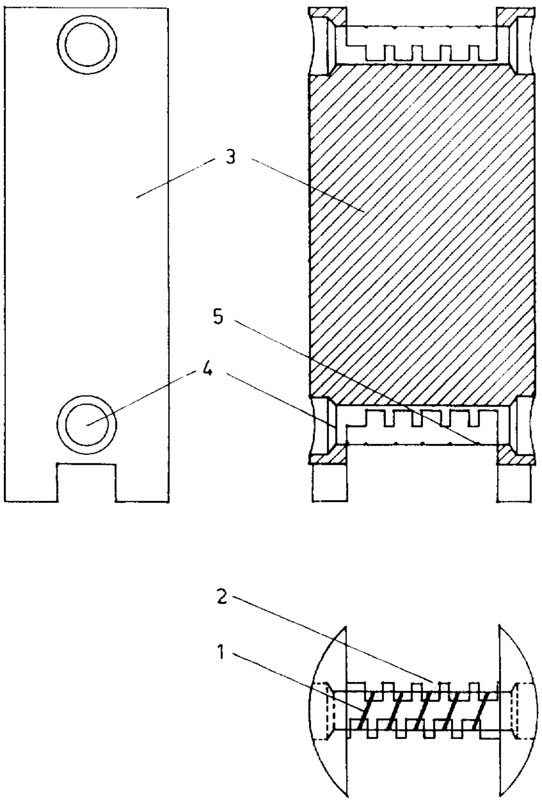

Fig. 7. First new sensitive element design: 1 = coil; 2 = channels for gas cavities; 3 = body; 4 = insulating pegs; 5 = helical grooves.

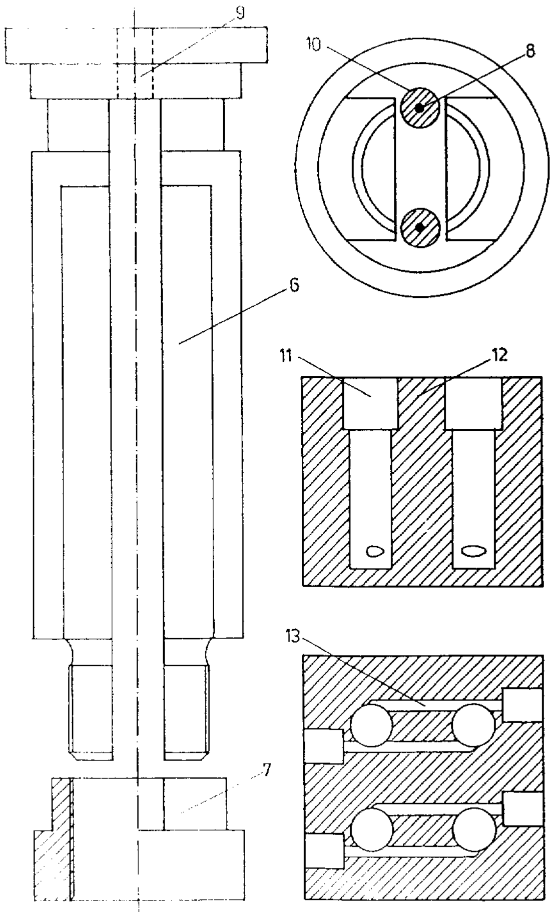

Fig. 8. First new sensitive elements design (continued): 6 = base; 7 = nut; 8 = leads; 9 = perforations; 10 = insulators; 11 = nests for sensitive elements; 12 = TCD block; 13 = channels for gas flows.

adverse "heat capacity effect" is decreased, while the additional inherent split among the channels 2 improves the TCD response time.

In the second TCD sensitive element design developed, which corresponds to version 2 in Fig. 6 and is shown in Fig. 9, coil 1 of radius 1.1 mm is situated around the central lead 3 of radius 0.4 mm including a 0.1 mm thickness of the insulator 2. Sagging and vibrations of the coil can be prevented through the three PTFE holders 4, by applying PTFE to the whole filament 5 or by coiling it twice in the manner shown in Fig.

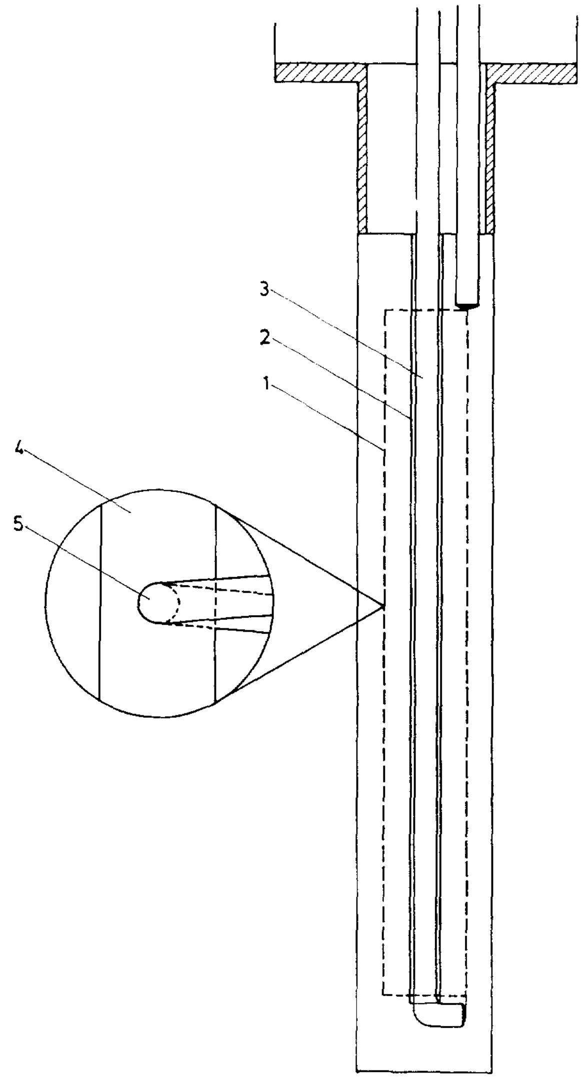

Fig. 9. Second new sensitive element design: 1 = coil; 2 = insulator; 3 = central lead; 4 = PTFE holders; 5 = filament.

10, where the primary spiral is of $r_s = 200$ μm and $h_s = 125$ μm, which parameters are technologically accessible and practically suitable, while the secondary sensitive element spiral is of $r_s^{max} = 1.1$ mm and $h_s = 1$ mm.

4. Conclusions

The analytical and numerical estimations presented allow the conclusion that in both one-

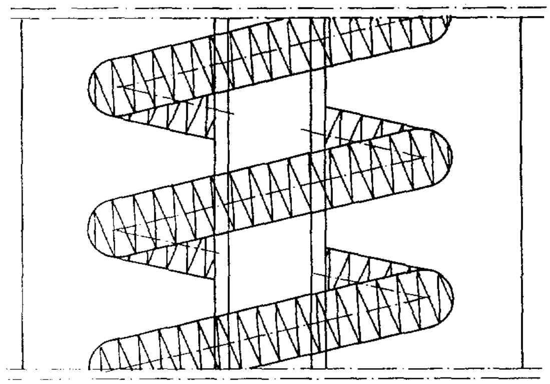

Fig. 10. Second new sensitive element design with a twice-coiled filament.

and two-way heat conduction the TCD sensitive element design can be optimized by using the appropriate spiral pitches and radiuses obtained. The positive effect of the hot-wire sensitive element design optimization on the TCD performance is additionally enhanced by the significant increase in the filament resistance provided. Further, the quantitative estimations show that the filament resistance at 0°C can be increased to 500–700 Ω if the ultimate capabilities of modern electronics are utilized in the d.c. sources needed for a TCD. Finally, the practical problems of the TCD performance improvement presented can be solved by the development of new optimized designs of high-resistance hot-wire sensitive elements, which could improve more than tenfold

Fig. 11. Photograph of first new design developed after the schematic drawings shown.

the performance of the "classical" TCD used in gas chromatography and in the other methods employing thermal conductivity phenomena for the measurement, analysis and control of volatile substances.

Fig. 11 shows the first new design developed.

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