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INFLUENCE OF THE TEMPERATURE FIELD ON A PERMITTIVITY DETECTOR IN LIQUID CHROMATOGRAPHY

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SUMMARY

A dual detector, based on a heterodyne principle with two variable oscillators, reacts both to observed changes in the real component of the complex permittivity and to a range of interferences. The most significant interference is caused by temperature fluctuations, and its analysis leads to an electrical equivalent diagram of the circuit of the detector. The analysis shows the requirements for the optimal arrangements of electrical, thermal and hydraulic relationships. These requirements were considered in the construction of the permittivity detector, with the help of which a sensitivity for the volume fraction $m_x \approx 3 \cdot 10^{-6}$ of benzene in *n*-heptane was achieved.

INTRODUCTION

Changes in the real component, ϵ' , of the complex permittivity are used for the detection of substances eluted at the outlet of the separation column of a liquid chromatograph. The permittivity detector developed operates with two radiofrequency oscillators, the frequency of which is influenced by the value of ϵ' of the dielectric that

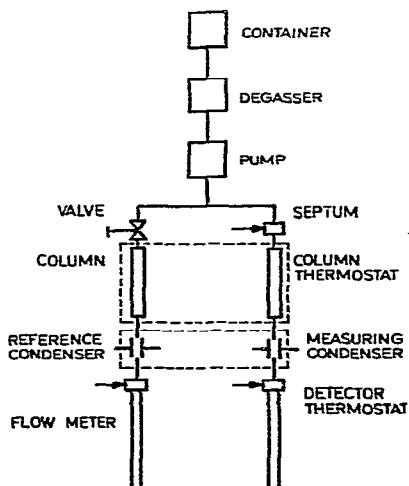


Fig. 1. Parallel arrangement of hydraulic circuit.

fills the flow-through condenser at a particular moment. According to the parallel configuration in Fig. 1, the eluent, together with the gradually eluted substances, flows through the measuring condenser in the right arm, whereas in the left arm the eluent alone flows through the reference condenser.

Fig. 2 shows a block diagram of the detector with two oscillators, O_1 and O_2 , whose frequencies, f_1 and f_2 , are influenced by the flow-through condensers C_1 and C_2 . High-frequency voltages from the separating amplifiers, Z , are brought to the frequency mixer, S , and to the low-frequency filter, F , behind which the converter, f/U , and the chromatogram recorder with the suppressing voltage source¹⁻³, K , are connected.

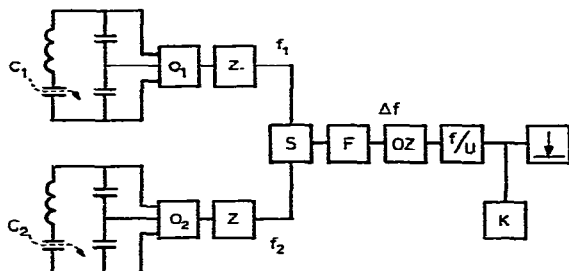


Fig. 2. Diagram of heterodyne detector.

The detector should reach the highest possible sensitivity towards changes in ϵ' with peaks lasting approximately 1 sec, which is why the working frequency of the oscillators was set at *ca.* 50 MHz.

INSTRUMENTATION

Interfering influences on the permittivity detector

Apart from the desirable changes in frequency, there are also further influences that create noise and zero drift. Increases in the detector sensitivity are usually limited by these particular interfering influences, the most significant of which are fluctuations in the electrical parameters and in the temperature.

To exclude the interfering influences, an arrangement is required that effects their stabilization, and in which the electrical equivalent diagram of the interferences in the detector can be considered as a parametrically balanced bridge, while on the other hand the equivalent diagram of the circuit with a measured value can be represented by an unbalanced bridge, the output of which represents the chromatogram on the recorder.

Equivalent thermal circuit

To acquire an idea of the features of a thermal circuit of the detector, which is not easy to survey, it is useful to employ an analogy with an electric circuit. An electrical equivalent connection is used for this purpose, with elements representing the elements of the thermal circuit.

In this analogy, the thermal leakage (equal to the reciprocal of the thermal resistance) is represented by the conductivity, G , and the thermal flow, $(dQ/dt)_{\text{term.}}$

where Q is the quantity of electricity, is represented by the flow of the electric current, I_{el} :

$$I_{el} = \left(\frac{dQ}{dt} \right)_{el} \approx \left(\frac{dQ}{dt} \right)_{term.} \tag{1}$$

The driving force of the thermal flow is formed by the temperature gradient ($T_2 - T_1$), represented by the difference in electrical potential ($E_2 - E_1$), or the electrical voltage, U (V):

$$U_{el} = (E_2 - E_1)_{el} \approx (T_2 - T_1)_{term.} \tag{2}$$

The electrical conductivity, G , which is equivalent to $1/R$, corresponds to the thermal conductivity:

$$G_{el} = \frac{I}{U} \approx \frac{dQ}{(T_2 - T_1) dt_{term.}} \tag{3}$$

Fig. 3a shows an electrical equivalent diagram of a thermal circuit of a heterodyne detector. The diagram is slightly simplified; it does not include the temperature dependences of either the oscillator coil or the transistor and other circuit elements. Capacitances C_v and C_n represent the thermal capacities of the flow-through condensers in the oscillator circuits. G_1 represents the thermal leakage between the condenser and the transistor as a source of heat; G_2 represents the thermal leakage between the condenser and the outer parts, which are formed mainly by the capillaries for the inlet and outlet of liquid. The conductivity G_3 represents the thermal leakage between the measuring condenser and the heating element.

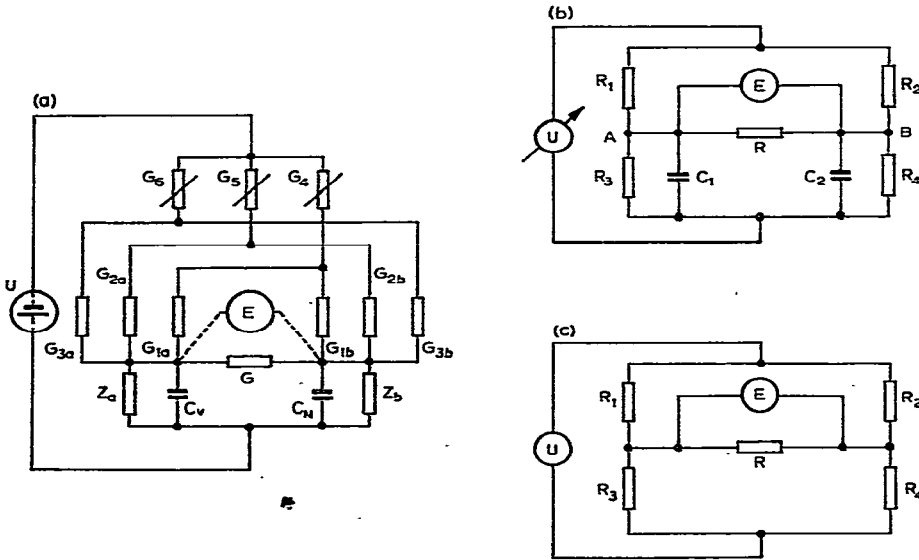


Fig. 3. (a) Electrical equivalent diagram of the thermal circuit. (b) Simplified equivalent diagram. (c) Equivalent diagram for the stabilized state.

The thermal situation of the arm with the measuring condenser, designated with a subscript a , is similar to the situation of the arm with the reference condenser, designated with a subscript b . Conductivities G_4 , G_5 and G_6 represent the routes of the thermal interference as variable thermal leakages, common to both bridge arms connected to the hypothetical source of the temperature difference U . For the detector it is assumed that the temperature of the condensers is higher than that of the surroundings. In practice, this means an essential simplification of the whole chromatograph. Conductivities Z then represent the thermal losses of the condensers into the surroundings, through which all of the heat brought into the condensers by means of G_1 , G_2 and G_3 is drawn off. Most of the heat is drawn off through the walls of the detector box, by analogy designated as leakages Z_a and Z_b .

It follows from the equivalent diagram that the disturbance interferences affect both thermal capacitances C_v and C_N symmetrically only when the capacities and their respective leakages are symmetrical. Thus $C_v = C_N$, $G_{1a} = G_{1b}$, $G_{2a} = G_{2b}$, $G_{3a} = G_{3b}$ and $Z_a = Z_b$. The thermal leakage, G , between C_v and C_N , *i.e.*, between the flow-through condensers, should be as high as possible, so that only a negligibly small temperature gradient would arise on it due to the equalizing thermal flow.

If the thermal leakages are symmetrical, the electrical equivalent diagram can be simplified as shown in Fig. 3b, which is valid for variable interferences and a dynamic state. Fig. 3c is even more simplified, and shows the stabilized state where the thermal capacities can be neglected. It follows from these illustrations that there is a temperature difference in the capacities of the condensers between points A and B. However, the value of the temperature difference is constant, and equal to zero, only when the thermal bridge is balanced:

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad (4)$$

If for the leakages

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} = 1 \quad (5)$$

and for the capacitances

$$C_1 = C_2 \quad (6)$$

then the balance and the zero difference in the condenser temperatures is also maintained under unstable conditions caused by the variable power source.

Arrangement for optimal thermal stability

It is important that the eventual changes in temperature should be nearly zero and very slow. Their time constant, $\tau = RC$, depends on the values of the capacity and the resistor through which the capacity is fed. If there is a resistor of resistance R_3 (namely the thermal leakage Z_a) connected parallel to the capacitance C_1 , the effective resistance decreases to a value given by the resistances of the parallel-connected resistors R_1 and R_3 . The time constant then is

$$\tau = C \cdot \frac{R_1 R_3}{R_1 + R_3} \quad (7)$$

In order to acquire very slow temperature changes, it is necessary to reach the minimum thermal loss leakage, Z , which corresponds to a maximal R_3 , which requires very good thermal isolation against the surroundings. A low voltage of the condenser C in the equivalent electrical circuit corresponds to a low degree of heating of the detector, and this can be acquired with the given thermal leakage R_3 with the help of the large resistance R_1 that corresponds to a low thermal input. As the result of the requirement of an equivalence of temperatures of both flow-through condensers, there arises the necessity for an efficient thermal leakage between the condensers C_V and C_N . They should be placed on a plate of good thermal conductivity, as close to each other as possible.

Changes in temperature of the flow-through condensers of both oscillators occur in two ways: by the influence of the linear expansion of the material on the one hand, and by the influence of the temperature dependence of the permittivity of the liquid that is filling the condenser on the other.

If we assume that only small temperature changes occur, so that the temperature dependences can be taken as linear, than the term for the condenser capacity is as follows:

$$C = \varepsilon_r' C_V \quad (8)$$

where ε_r' is the real component of the relative complex permittivity of the measured liquid and C_V is the capacity of the empty measuring condenser.

The influence of the temperature change from T_0 to T is expressed by

$$C_V = C_{V_0} [1 + TK_c (T - T_0)] \quad (9)$$

$$\varepsilon_r' = \varepsilon_{r_0}' [1 + TK_{\varepsilon'} (T - T_0)] \quad (10)$$

where

$$TK_c = \frac{dC}{C dT} \text{ (}^\circ\text{K}^{-1}\text{)} \quad (11)$$

is the temperature coefficient of the capacity of the empty condenser, which is dependent on the construction and the materials used.

$$TK_{\varepsilon'} = \frac{d\varepsilon_r'}{\varepsilon_r' dT} \quad (12)$$

which is the temperature coefficient of the liquid that is filling the condenser.

By substituting eqns. 9 and 10 into eqn. 8, we obtain

$$C = \varepsilon_{r_0}' C_0 [1 + TK_c (T - T_0) + TK_{\varepsilon'} (T - T_0) + TK_c TK_{\varepsilon'} (T - T_0)^2] \quad (13)$$

For low values of TK_c and TK_{ε}' , it is possible to neglect the square at the end of the eqn. 13 and we obtain

$$C \approx \varepsilon_{r_0}' C_0 [1 + (TK_c + TK_{\varepsilon}') (T - T_0)] \quad (14)$$

The condenser capacity thus depends on the sum of the temperature coefficient of the empty condenser and that of the real component of the complex permittivity of the liquid.

The real relationships are more complicated⁴, but the result of this problem, however, remains essentially the same.

It is possible to give some actual data for the temperature coefficients. The real components, ϵ'_r , of the complex permittivity of some substances (otherwise the dielectric constant) and the temperature coefficients, $TK_{\epsilon'}$, for the change of ϵ' with temperature are given in Table I.

TABLE I
TEMPERATURE COEFFICIENTS FOR SOME AROMATIC COMPOUNDS

Compound	$\epsilon'_r (20^\circ\text{C})$	$TK_{\epsilon'} = \frac{d\epsilon'}{\epsilon' dT}$
Cyclohexane	2.0148	$7.796 \cdot 10^{-4}$
Benzene	2.2463	$7.158 \cdot 10^{-4}$
Chlorobenzene	5.6895	$3.059 \cdot 10^{-3}$
Nitrobenzene	35.72	$5.180 \cdot 10^{-3}$

The temperature coefficient of the capacity of the empty condenser was measured on samples of coaxial flow-through condensers. With the brass type it was found that $TK_c = 1.60 \cdot 10^{-3} \text{ }^\circ\text{K}^{-1}$, while for a coaxial condenser made of chrome stainless steel, type 17022, $TK_c = 3.0 \cdot 10^{-4} \text{ }^\circ\text{K}^{-1}$.

A comparison of TK_c with $TK_{\epsilon'}$, shows that both temperature dependences affect the measuring error to nearly the same extent, which is why it is important to devote attention to decreasing TK_c by using a suitable construction of the condenser and to stabilize carefully the detector temperature in order to restrict the influence of both temperature coefficients.

Arrangement for optimal electrical stability

Changes in temperature are the cause of the fluctuation of the capacity and also of the output detector signal, although they are not the only cause. The dependence of the oscillator frequency on the supply voltage and on the electrical symmetry of both oscillators is also significant. Apart from this, such electrical asymmetry causes an asymmetry of the Joule heat, which in turn leads to temperature asymmetry. For this reason, it is advisable to secure symmetry and stability of the detector not only by its design but also by setting identical inputs during its operation.

Arrangement for optimal hydraulic relationships

The influence of interference factors has already been discussed; their suppression requires a symmetrical bridge arrangement. Should such an arrangement of the detector lead to better stability and sensitivity, the symmetry must be retained with considerable care in all respects: geometrically, electrically, thermally and also in the liquid flow that causes thermal effects.

Requirement of temperature stability

As has been derived before, the temperature coefficient of the condenser capacity and also of the real component, ϵ' , of the complex permittivity of the substances under consideration are $TK \approx 10^{-3} \text{ (relative) }^\circ\text{K}^{-1}$.

If there are changes ϵ' with a sensitivity of, e.g., 10^{-6} (relative) to be followed by the detector, then the temperature should not fluctuate by more than

$$\Delta T = \frac{\Delta \epsilon'}{\epsilon' TK} = \frac{10^{-6}}{10^{-3}} = 10^{-3} \text{ } ^\circ\text{K}$$

Owing to the symmetrical bridge arrangement, the real factor demanded is lower; however, in spite of this the requirement of increasing sensitivity leads to the need for temperature stabilization in the region of a few thousandths of a degree.

Arrangement of the chromatograph

In contrast to Fig. 1, a series hydraulic arrangement of the chromatograph with two separately thermostated boxes is shown in Fig. 4. The mobile phase flows from the container through the thermal degasser, through a pump and the pulse damper, to the filter and the needle valve, with the help of which the liquid flow is adjusted. The mobile phase enters the column thermostat, the heat exchanger and the saturation column, from where it passes into the detector thermostat and into the reference flow-through condenser. From there it returns through the column thermostat for feeding the sample. Then it enters the separation column, the measuring flow-through condenser, then again through the thermostat to the flow meter and out.

In order to attain good symmetry, both flow-through condensers are connected to the inlet and outlet capillaries that serve at the same time as heat exchangers in the thermostat. For better heat transfer a special silicone vaseline (Unisilicon TK SBA,

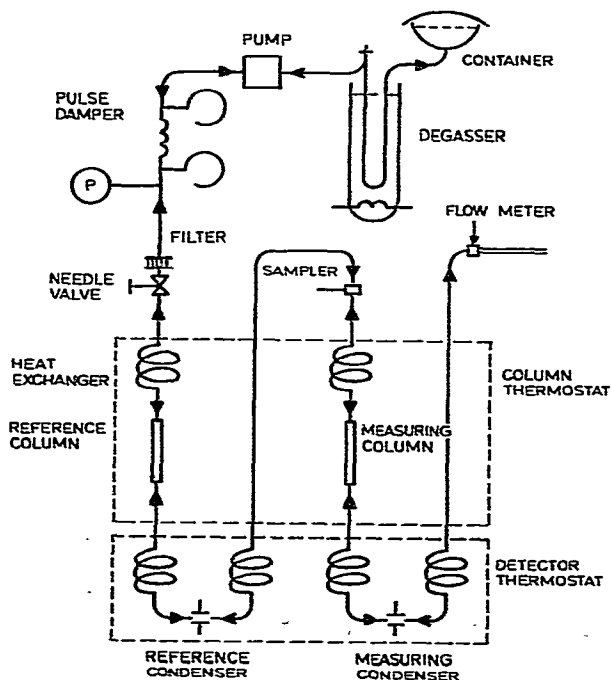


Fig. 4. Liquid chromatograph with detector condensers.

Klüber Lubrication, Vienna, Austria) with good thermal conductivity is used, being coated between the surface of the capillaries and the copper block of the thermostat.

Detector

It was our aim to achieve the best possible stability of the output signal while maintaining the optimal thermal, electrical and hydraulic stability.

The electrical input of the oscillator was reduced in the all-transistor concept of the detector to 20 mW, which is *ca.* 100–1000-fold less than in a similar electron-tube version². Both oscillators were of the Clapp-type, with separator stages, and a mixer with a stabilized power supply for the thermistor bridge. The total input of the detector parts built in a copper block with a mass of 5300 g was 1.5 W. The copper block, together with the heating elements covering both opposite walls, is placed in an isolation case made of polystyrene foam with external dimensions of 140 × 165 × 200 mm.

Temperature controller

The detector is thermostated by a commercial controller, Type DHS (Eurotherm, Worthing, Great Britain). It is a universal transistor controller with adjustable PID* (three-term controller), adjustable maximum output and reference voltage set in four decade switches with a resolution of 2 μ V. The controller also contains an auxiliary disturbance compensator that quickly compensates the fluctuation of the line voltage before it causes temperature changes.

The inlet of the regulator is connected to the outlet of a Wheatstone bridge with a thermistor, Type NRZ 1001.3K/EI-R (Pramet, Šumperk, Czechoslovakia). Its exchangeability is better than 1 °C.

The power supply for the thermistor bridge is stabilized by a zener dipole (Tesla KZZ82), which is placed together with the Manganin resistors of the bridge in the thermostated case of the detector. The setting of the proportional term of the controller was optimal when the stabilization coefficient of the whole regulation circuit was 2100.

RESULTS

The whole power consumption of the detector causes a temperature rise of not more than 5 °C, so that even in summer it is possible to work with this detector at the highest temperature of 35 °C without using any cooling system. This leads to the advantage of a simple temperature control⁵ without cooling, even for studying biological materials.

Under these conditions, the fluctuation of the block temperature was measured with the help of a platinum resistance miniature sensor (Type P3, Degussa, Hanau, G.F.R.). Fig. 5 shows the recording of the temperature of the detector with a sensitivity of 0.003 °K/mm. Ten minutes after switching on, the temperature was stabilized within an error of 0.01 °K and after approximately half an hour the temperature was steady with a hardly noticeable fluctuation of less than 10⁻³ °K.

* PID = Proportional Integral Derivative.

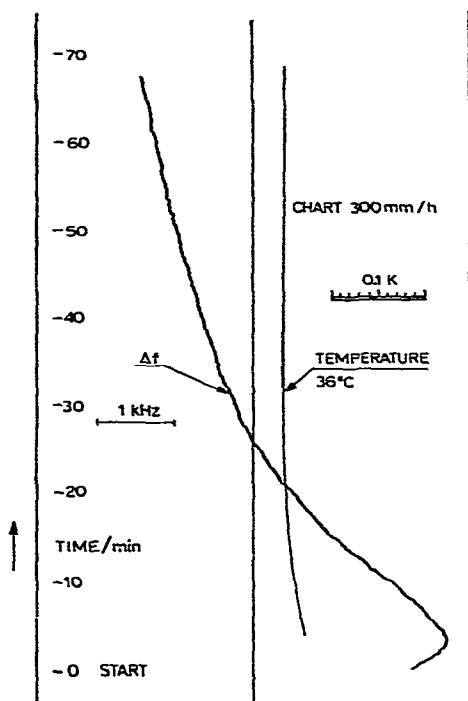


Fig. 5. Recording of temperature and frequency drift.

The other line represents the output signal of the detector. Its drift lasts slightly longer than the temperature stabilization.

The operating model of this detector was constructed without the use of any contact surface protection. Under good conditions there was a noise of less than ± 7 Hz. Holding that the smallest detectable peak is twice as great as the noise band, the smallest detectable volume fraction of benzene in *n*-heptane is $m_x = 3 \cdot 10^{-6}$ (relative).

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