PERMITTIVITY AND CONDUCTIVITY DETECTORS FOR LIQUID CHROMATOGRAPHY

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SUMMARY

A critical review is given of methods and devices concerning a new family of liquid chromatographic detectors based on electrical conductivity and either component of the complex permittivity as physical quantities depending on the concentration of the compounds being analyzed. Two new detectors are suggested: a self-balancing capacitance detector and a self-balancing resonance detector.

INTRODUCTION

The task of the detector in liquid chromatography (LC) is to furnish a d.c. electrical signal that is proportional to the concentration of a substance being analyzed in a binary mixture on the chromatograph column output.

As in gas chromatography, two primary qualities are required in detectors in liquid chromatography, namely, high sensitivity and linearity over a wide range of concentrations. Lately, two types of detector have found widespread use: the ultraviolet (UV) detector and the differential refractometer (DR). The interaction of the electromagnetic waves with the molecules of a liquid mixture under analysis is employed with both of these detectors. The absorption of radiation energy in the ultraviolet region is utilized with the UV detector, whereas a change in the refractive index in the visible region is used with the differential refractometer. An evaluation has been made recently[1].

There has been a tendency to utilize gas chromatographic detectors, particularly the more sophisticated detectors, in liquid chromatography. In particular, the high sensitivity of modern flame ionization detectors (FID) seemed to be very attractive, and detectors have been designed in which the evaporated mixture is subjected to detection with an FID[2].

However, in order to utilize to their full extent the excellent potentialities of modern liquid chromatographic columns, special LC detectors have to be developed, based on earlier designs[3–5].

CONDUCTIVITY AND PERMITTIVITY AS VARIABLES

One can readily derive an equation for the electrical current density, $\vec{J}$, from the first Maxwell equation:

$$\vec{J} = g \cdot \vec{E} + j \cdot \omega \cdot \varepsilon^* \cdot \vec{E} \tag{1}$$

where

$\vec{J}$ = density of electrical current $(A \cdot m^{-2})$;
g = electrical conductivity $(S \cdot m^{-1})$;
$\vec{E}$ = intensity of harmonic electrical field $(V \cdot m^{-1})$;
ω = angular frequency of the field $(rad \cdot sec^{-1})$

and

$$\varepsilon^* = \varepsilon' - j \cdot \varepsilon'' \tag{2}$$

the complex permittivity with the real and imaginary components ε' and ε'', respectively.

A stationary dielectric medium is assumed in eqn. 1. However, this is not the case with the detector capacitor in LC, where the analyzed liquid mixture is flowing through the capacitor with a velocity $\vec{v}$.

If we denote by F the force acting on a stationary point charge q, then

$$\vec{F} = q \cdot \vec{E} \tag{3}$$

If the dielectric medium is moving with a velocity $\vec{v}$, then the force acting on a point charge will be given by

$$\vec{F} = q \cdot (\vec{E} + \vec{v} \cdot \mu \cdot \vec{H}) \tag{4}$$

The effect of the motion of the dielectric particles is the same as when an effective field intensity

$$\vec{E}_{eff} = \vec{E} + \vec{v} \cdot \mu \cdot \vec{H} \tag{5}$$

acts on a stationary dielectric.

It can be derived that the magnetic field in the space between the capacitor electrodes is parallel to the electrodes, and its magnitude is just equal to the magnitude of the surface current density on the plates[6].

Because of the risk of dielectric heating of the liquid, small current densities must be applied, particularly if thin layers of liquid are used.

Also, the velocities, $\vec{v}$, of the liquid mixture are very low with low-volume capacitors. Therefore, the effect of motion on the current density can be neglected, and eqn. 1 will be accepted in further treatments.

Changes in g, ε'' and ε', due to the presence of an analyzed component in a liquid carrier, must be converted into an electrical signal. Therefore, a capacitor, passed through by the binary mixture, is attached to the LC column output, as a sensor.

Very thin layers of liquid must be employed between the electrodes of the capacitor, because of the necessity to have a small internal volume, and therefore the gradient components along the electrodes will be zero. Assuming also that there is a uniform distribution of the concentration along the layer, a uniform current distribution over the electrode surface can be assumed and an equation can be written for the gradient:

$$\vec{E} = -\text{grad } \vec{U} = \frac{\vec{U}}{d} \tag{6}$$

Substituting in eqn. 1 and multiplying by the effective electrode area, S, we obtain for harmonic electric current through the capacitor:

$$\vec{I} = (g + \omega\varepsilon'') \cdot \frac{S}{d} \cdot \vec{U} + j \cdot \omega \cdot \varepsilon' \cdot \frac{S}{d} \cdot \vec{U} \tag{7}$$

Use of the relative permittivity is advantageous:

$$\varepsilon = \varepsilon_r \cdot \varepsilon_0 \tag{8}$$

and, substituting in eqn. 2:

$$\varepsilon^* = (\varepsilon'_r - j \cdot \varepsilon''_r)\varepsilon_0 \tag{9}$$

where ε_0 is the permittivity of a vacuum ($\varepsilon_0 = 10^{-9}/36\pi$) ($\text{F} \cdot \text{m}^{-1}$). However, the following equation holds, approximately, for the empty capacitor:

$$C_0 = \varepsilon_0 \cdot \frac{S}{d} \qquad (\text{F}; \text{m}^2; \text{m}) \tag{10}$$

and, finally, for the current through the detector capacitor:

$$\vec{I} = (g/\varepsilon_0 + \omega\varepsilon''_r) \cdot C_0\vec{U} + j\omega\varepsilon'_r \cdot C_0\vec{U} \tag{11}$$

Supposing a linear response of the electrical channel used for the signal processing, it is necessary that the variable used is a linear function of concentration of the substance to be detected in the carrier liquid. This requirement is fulfilled with a high accuracy with the real component of the relative complex permittivity ε'_r, since it holds:

$$\varepsilon'_{rr} = (1 - m_x)\varepsilon'_{rc} + m_x \cdot \varepsilon'_{rx} = \varepsilon'_{rc} + m_x(\varepsilon'_{rx} - \varepsilon'_{rc}) \tag{12}$$

where

ε'_{rr} = resultant real component of the relative complex permittivity, ε^*_{rr}, of the binary mixture;

ε'_{rc} = real component of the relative complex permittivity of the carrier;

ε'_{rx} = real component of the relative complex permittivity of the substance to be detected;

m_x = concentration of the substance to be detected in the carrier in volume fraction.

It follows that there is an analogy between the differential refractometer, using the change in the refractive index, n, on the one hand, and the permittivity detectors utilizing the change in ε'_r, on the other hand, because of the relationship

$$\varepsilon'_r = n^2 \tag{13}$$

Similarly, there is an analogy between the UV detector in the UV region of electromagnetic waves, and conductance detectors based on the dissipation of energy in the radio-frequency region of electromagnetic waves.

FLOW-THROUGH CAPACITOR AS A SENSOR

The sensing capacitor is to be regarded as an extremely important element that affects considerably the performance of the detection system. The main requirements for its design and properties can be summarized as follows: small internal volume; laminar flow; avoidance of gas cushions; tightness against leakage; stability of capacity; low constant capacity; low temperature coefficient of capacity; possibility of precise thermostating; uniform liquid layer; homogeneous field distribution; electrical shielding; low residual parameters; and anticorrosive construction. The first two requirements are closely connected with the necessity to avoid a wash-down of the chromatographic zones (peaks) on the column output[1,7]. Careful design in order to obtain laminar flow, and an internal volume not exceeding about 10 μl are required.

The repeatibility and reproducibility of analysis assume, in addition to other requirements, that the effective electrode area remains constant within a series of analyses. This postulate can, however, be seriously endangered by the build-up of air or vapour cushions between the electrodes. Therefore, the liquid inlet should be located at the lowest point and the outlet at the highest point of the capacitor cavity. Also, degassing of the liquid carrier is important.

A good seal against liquid leakage and the stability of capacitance depend mainly on the material used as a solid dielectric for the electrode spacing and for tightness. As low-viscosity solvents are very often used as the carrier, a soft material must be applied as the seal. The use of PTFE as the seal is advantageous and, in addition, its radio-frequency losses are very low, but it is subject to creeping under stress, which reduces the long-term stability of the capacitance. Designs that involve the use of more stable materials for spacing (ceramics or molten quartz) and PTFE as the seal, are to be preferred, as a high long-term stability of the capacitance can be attained.

The capacitance of every flow-through capacitor consists of two components: a wanted variable capacitance, C_v, caused by an electric field through the liquid dielectric, and an unwanted constant capacitance, C_k, caused by an electric field through the solid dielectric. The unwanted constant capacitance can be kept low by decreasing the respective electric field, $i.e.$ by increasing the thickness of the solid dielectric in the direction of electric gradient.

The high efficiency of the LC analysis can be utilized in practice if an adequate zero-line stability of the chromatogram can be guaranteed. It has been shown both theoretically and experimentally that the influence of temperature on the capacitance

of the flow-through capacitor plays the main role. The following equation can be written for this capacitance:

$$C = C_k + C_v = \varepsilon'_r \cdot \varepsilon_0 \cdot \frac{S_k}{d_k} + \varepsilon'_{rc} \cdot \varepsilon_0 \cdot \frac{S}{d} \tag{14}$$

The temperature dependence of C_k can be neglected with respect to that of the variable capacitance, C_v, assuming a careful design, and the following equation can be written for the increment of capacitance, ΔC, due to a temperature change, $\Delta \Theta$:

$$C_v + \Delta C_v = (\varepsilon'_{rc} + \Delta \varepsilon'_{rc}) \cdot \varepsilon_0 \frac{S + \Delta S}{d + \Delta d} \tag{15}$$

and for the temperature coefficient of capacitance:

$$TK_c = \frac{1}{C_v} \cdot \frac{\Delta C_v}{\Delta \Theta} \tag{16}$$

or

$$\Delta C_v = C_v \cdot \Delta \Theta \cdot TK_c \tag{17}$$

Using analogous equations for the increments of other variables, we obtain

$$1 + \Delta \Theta \cdot TK_c = \frac{1 + \Delta \Theta (TK_s + TK_{\varepsilon'})}{1 + \Delta \Theta \cdot TK_d} \tag{18}$$

and, finally

$$TK_c = \frac{TK_s + TK_{\varepsilon'} - TK_d}{1 + \Delta \Theta \cdot TK_d} \tag{19}$$

Neglecting the term $\Delta \Theta \cdot TK_d$, with respect to unity:

$$TK_c = TK_s - TK_d + TK_{\varepsilon'} \tag{20}$$

or for

$$TK_c = 0 \tag{21}$$

$$TK_d - TK_s = TK_{\varepsilon'} \tag{22}$$

The temperature of the capacitor and of the carrier liquid must be maintained constant, even with a capacitor that has been very carefully designed. The requirement for a precise automatic tempering may seriously influence the design, particularly because of the need for easy disassembly in order to clean the cavity. The use of a servo system with thermoelectric batteries and cooling water is satisfactory.

The increment of capacitance due to temperature can be seen to be caused by change of dimensions (TK_s, TK_d) and changes in the permittivity of the carrier (TK). There is a need for a minimum value of the variable capacitance, C_v, to be used in electrical circuits for the conversion of the capacitor admittance change into a signal suitable for recording. A decrease in C_v also adversely affects the ratio C_v/C_k. However, a small internal value is also wanted and therefore a very thin gap between elec-

trodes must be used, a layer thickness of 0.05–0.10 mm often being employed. In order to obtain a good signal-to-noise ratio, there is a tendency to use as high as possible a voltage across capacitor. Its value is limited by two factors: the electrical break-down voltage and dielectric heating of the layer.

The break-down voltage is given by the gradient U/d. A value of 30 V (r.m.s. value) has been found to be satisfactory for layers of 0.05 mm with hexane.

The power dissipated in the liquid layer is given by the equation

$$P = G \cdot U^2_{r.m.s.} = (g/\varepsilon_0 + \omega\varepsilon''_r)C_0 \cdot U^2_{r.m.s.} = \omega C_v \cdot \text{tg } \delta \, U^2_{r.m.s.} \tag{23}$$

which gives rises to a heat:

$$Q = 0.24 \, P \cdot t = 0.24 \, (g/\varepsilon_0 + \omega\varepsilon'_r)C_0 \cdot U^2_{r.m.s.} \cdot t = \omega C \cdot \text{tg } \delta \, U^2_{r.m.s.} \cdot t \tag{24}$$

The volume density of the dielectric heat arising in the liquid is uniform across the layer, but heat transfer to cooler electrodes gives rise to a temperature distribution, as shown in Fig. 1, the highest temperature being about in the middle of the layer.
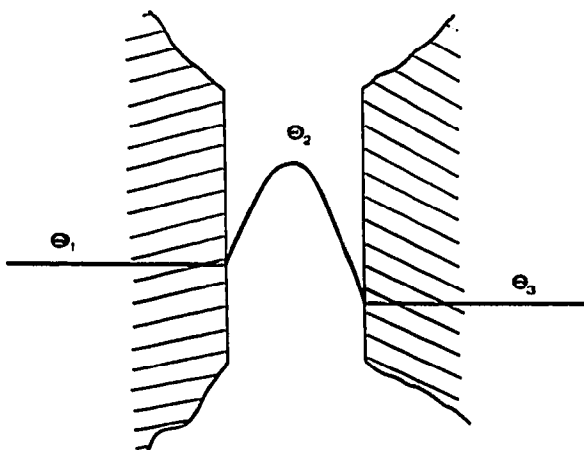

Fig. 1. Distribution of temperature across the capacitor.

Both limiting parameters, *i.e.* that given by the break-down voltage and that given by the dielectric heating, require a precise uniformity of the layer thickness to be guaranteed in the flow-through capacitor. Any inhomogeneity may cause either an increase in the voltage gradient or local overheating of the layer and, therefore, instability. The dissipated power is directly proportional to the frequency used and the danger of overheating therefore increases with the frequency. It may be objected that overheating cannot occur because of the near vicinity of cold electrodes. However, dielectric heating may result in only a thin interlayer becoming overheated or, with volatile substances, it can cause the decomposition of a substance.

As postulated in the theory of alternating electromagnetic fields, both components, *i.e.* the electric and the magnetic component, must be present in an electrical a.c. circuit. Because of the alternating magnetic and electric energy in the electromag-

netic field, dissipation of energy must also arise from this energy conversion (second law of thermodynamics), so that every capacitor must represent, in addition to a capacitance, also some inductance and resistance. These components of its impedance are called residual parameters and their influence increases with increase in the operating frequency used. In detector systems with lumped parameters and frequencies up to 10^7 Hz, a coaxial construction is satisfactory[4,5,8]. The design in Fig. 2 can be recom-
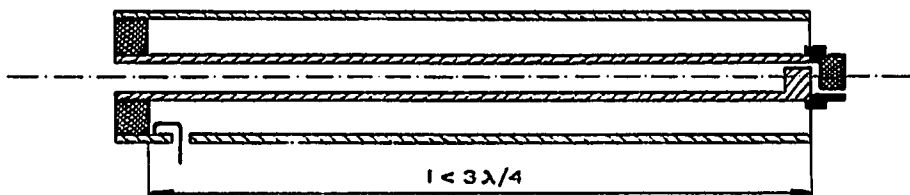

Fig. 2. Coaxial oscillating resonance circuit with flat circular-shaped capacitor.

mended for systems using frequencies of the order of 10^8 Hz. A short-circuited coaxial line, somewhat shorter than $3\lambda/4$, is used as the oscillating circuit tuned to resonance by the flow-through capacitor located at the hot end of the line. The liquid being analyzed flows through the internal conductor of the coaxial line. Internal volumes of $10\,\mu$l and less and capacitances of about 3–4 pF are readily attained.

Obviously, the detector capacitor must be protected against parasitic stray fields by shielding, and anticorrosive materials of construction must be used.

CONVERSION OF CHANGE IN ADMITTANCE INTO AN ELECTRICAL SIGNAL

The change in the admittance of the flow-through capacitor, caused by the presence of a compound being analyzed, must be converted into a d.c. signal convenient for a self-balancing line recorder or for digital treatment.

Eqn. 11 shows that two variables, at least, can be utilized for the design of detectors in liquid chromatography. With respect to the physical quantities used as variables, the detectors can be divided in three groups:

(1) detectors with a response to changes in the quadrature component of the capacitor admittance, i.e., to capacitance, $\omega\varepsilon'_r\cdot C_0$;

(2) detectors with a common response to both components, i.e., to changes in admittance;

(3) detectors giving separate signals for either component, $(g/\varepsilon_0 + \omega\varepsilon''_r)\cdot C_0$ and $\omega\varepsilon'_r C_0$.

However, there remains a further possibility for obtaining two separate signals for the components $g\cdot C_0/\varepsilon_0$ and $\omega\varepsilon''_r C_0$, for one is a function of frequency.

As the relationships among the variables g, ε'' and ε' and the frequency function, $F(\varepsilon'', \varepsilon')$, are characteristic of the constitution of the molecules of the compound to be analyzed, systems that give more than one chromatogram are to be preferred, for they may aid in the identification of the compound (selective detectors).

Because of the very small relative changes in the capacitor admittance due to very small concentrations that are to be detected, the system must be able to compensate the initial admittance, corresponding to a pure carrier liquid admittance, and,

therefore, to allow the use of a high sensitivity of the measuring channel and of the recorder. In this case, the signal is proportional to the changes in admittance components only; for example, in the case of capacitance:

$$\Delta\varepsilon'_r = \varepsilon'_{rc} + m_x(\varepsilon'_{rx} - \varepsilon'_{rc}) - \varepsilon'_{rc} = m_x(\varepsilon'_{rx} - \varepsilon'_{rc}) \tag{25}$$

that giving the change of capacitance:

$$\Delta C = \Delta\varepsilon'_r \cdot C_0 = \Delta\varepsilon'_r \cdot \varepsilon_0 \cdot \frac{S}{d} \tag{26}$$

Capacitance detectors

Heterodyne detectors. The principle well known in radioelectronics was utilized[5,8], as shown in Fig. 3.

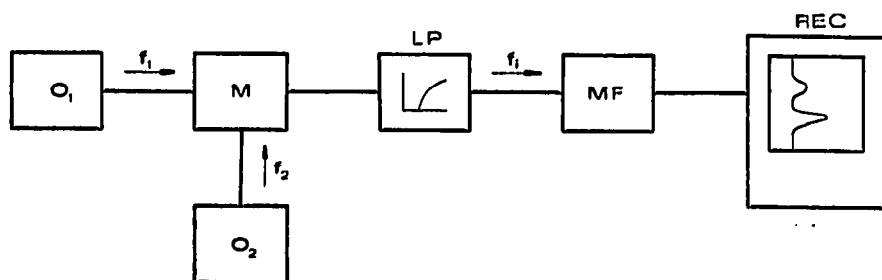

Fig. 3. Schematic diagram of ordinary heterodyne detector.

A constant frequency, f_1, of a quartz oscillator, O_1, is mixed in a mixer, M, with a variable frequency, f_2, from an oscillator, O_2, having a flow-through capacitor in its oscillating circuit. Assuming that a convenient value of the inductance, L, has been chosen, the oscillator O_2 may oscillate at a frequency, f_{2c}, equal to the frequency of the quartz oscillator, f_1, if a pure carrier liquid is flowing through, *i.e.*:

$$f_{2c} = \frac{1}{2\pi\sqrt{L}} \cdot \frac{1}{\sqrt{(C_c + C_k)}} = k \cdot \frac{1}{\sqrt{(C_c + C_k)}} = f_1 \tag{27}$$

where

C_c = capacitance of the flow-through capacitor with a pure carrier liquid;
C_k = constant capacitance in the oscillating circuit.
Owing to the presence of the detected compound, the capacitance C_c changes to C_r, and the frequency of O_2 changes to

$$f_{2r} = k \cdot \frac{1}{\sqrt{(C_r + C_k)}} \tag{28}$$

After filtering the high-frequency components, there remains, on a low-pass filter, LP, output, a signal having a frequency

$$f_1 = |f_{2c} - f_{2r}| = k \cdot \left(\frac{1}{\sqrt{(C_c + C_k)}} - \frac{1}{\sqrt{(C_r + C_k)}} \right) \tag{29}$$

This signal is converted into a d.c. signal that has a voltage proportional to the interference frequency, f_i, in the frequency meter, MF, for feeding the recorder, REC.

A detector involving the use of this principle was investigated by Vespalec and Hána[8], and Poppe and Kuysten[9]. Careful measurements showed that it gave sensitivities comparable with those of the differential refractometer over a large range of concentrations.

Some difficulties with heterodyne detectors lie in the necessity of using the oscillator O_2 over a wide frequency range, owing to the various solvents employed as carriers.

Self-balancing capacitance detectors. A circuit has been suggested[10] with an oscillator, O_2, tuned automatically to a frequency f_2 equal to f_1 of the constant frequency oscillator, O_1, by means of a Varicap. The d.c. signal needed for the Varicap control is recorded. The system is shown schematically in Fig. 4. The phase
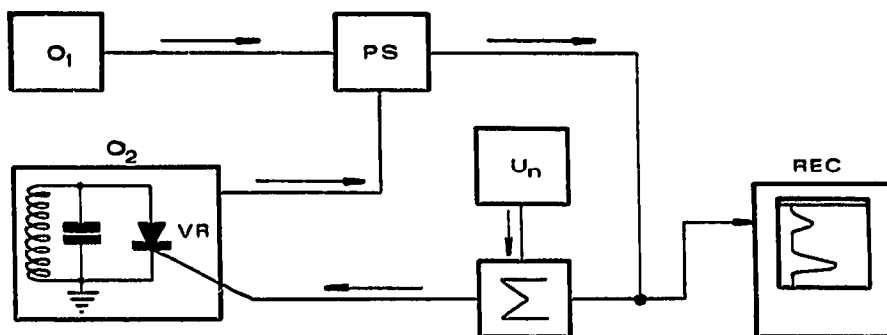

Fig. 4. Schematic diagram of self-balancing capacitance detector.

angle of the signal from the constant frequency quartz oscillator, O_1, is compared in a phase-sensitive detector, PS, with that of the signal from the oscillator O_2, which has a flow-through capacitor in the oscillating circuit. The signal on the PS output is utilized to control the capacitance of Varicap, VR, in such a way that the frequency of O_2 remains constant and equal to the frequency of the quartz oscillator, O_1. The control signal for the Varicap, if used within the linear section of its characteristic, is a linear function of the change in concentration of the compound being analyzed, and is recorded by the recorder, REC. Adjustment of the zero line is achieved with an adjustable d.c. voltage from the stabilized source, U_n, that is superimposed to control the signal as a bias for Varicap, VR, in the block Σ.

The heterodyne and self-balancing detectors are very sensitive to changes in ε'_r, but cannot be used with liquid mixtures that have higher conductivities, as the conductance component of the capacitor admittance causes a damping of the resonant circuit and, therefore, an instability of the oscillations of oscillator O_2.

Admittance detectors

As has been shown in eqn. 23, the sensitivity of the detector to the presence of an analyzed compound in a liquid carrier depends on the difference in the magnitudes of the physical properties of the carrier and of the compound to be detected. Com-

pounds that have nearly the same ε'_r values (dielectric constant) as that of the solvent which is used as the carrier give low sensitivities.

Therefore, the possibility of using the slope of the resonance curve with such compounds has been examined[4], with the aim of utilizing a very high sensitivity of the amplitude of oscillations in a low-loss resonant circuit for damping, caused by dissipation of energy. The chromatogram of a detector based on this principle represents a common response to both of the variables $(g/\varepsilon_0 + \omega\varepsilon''_r)C_0$ and $\omega\varepsilon'_r C_0$.

Detectors involving the resonance principle have been further investigated with the aim of obtaining two separate chromatograms, as will be shown elsewhere[11].

Detectors giving two separate chromatograms

As has been already stated, a detector that gives two separate chromatograms, *i.e.*, for the conductance component and for the quadrature component of the detecting capacitor admittance, the capacitance, is to be preferred. With respect to the magnitude of the conductance component $(g/\varepsilon_0 + \omega\varepsilon''_r)C_0$, detectors of this group can be divided into a.c. bridge detectors and resonance detectors.

Self-balancing a.c. bridge detector. Sensitive direct-reading automatic a.c. bridges may be utilized, in connection with a flow-through capacitor, as liquid chromatographic detectors for compounds with higher conductance components. In order to obtain two separate chromatograms only automatic bridges are suitable, giving two separate signals for the conductance and capacitance components.

From the point of view of extracolumn zone broadening, it is very convenient if the flow-through capacitor may be located immediately adjacent to the column outlet. Taking this into account, a detector was developed based on the principle of a self-balancing current transformer bridge[12]. It was shown[5] that the admittances of coaxial cables, for connecting the detecting capacitor to the bridge device, do not influence the readings, one cable having either the internal or external conductor very nearly at zero potential, the other cable influencing either current branch of the bridge to the same extent.

The greatest advantage of this auto-balanced bridge lies in its capability of giving two separate signals for either component of the admittance. The detector is shown schematically in Fig. 5. The flow-through detecting capacitor, C_{det}, connected in the lower current branch is balanced manually for a pure carrier to zero output on the secondary winding of the current transformer, T_1, coarsely switching the taps on the transformer, and finally by adjusting the voltages on the potentiometers, P_1 and P_2. The balancing must be done in both components, either with respect to the built-in standards, G_n and C_n, or against another capacitor through which a pure carrier flows.

A signal, arising from the imbalance caused by an analyzed compound, is amplified in an electronic amplifier, EA, and used for rebalancing the bridge by means of an auxiliary magnetic flux produced by a control winding, CW. The separation of the admittance components, $(g/\varepsilon_0 + \omega\varepsilon''_r)C_0$ and $\omega\varepsilon'_r C_0$, is obtained by means of two phase-sensitive detectors, PS_1 and PS_2, one being connected to the output of a 90° phase-shifter.

Self-balancing resonance detector[11]. There is a need, in liquid chromatography, to analyze liquid mixtures covering a large number of very different substances, particularly organic compounds. The above detectors are capable of detecting many
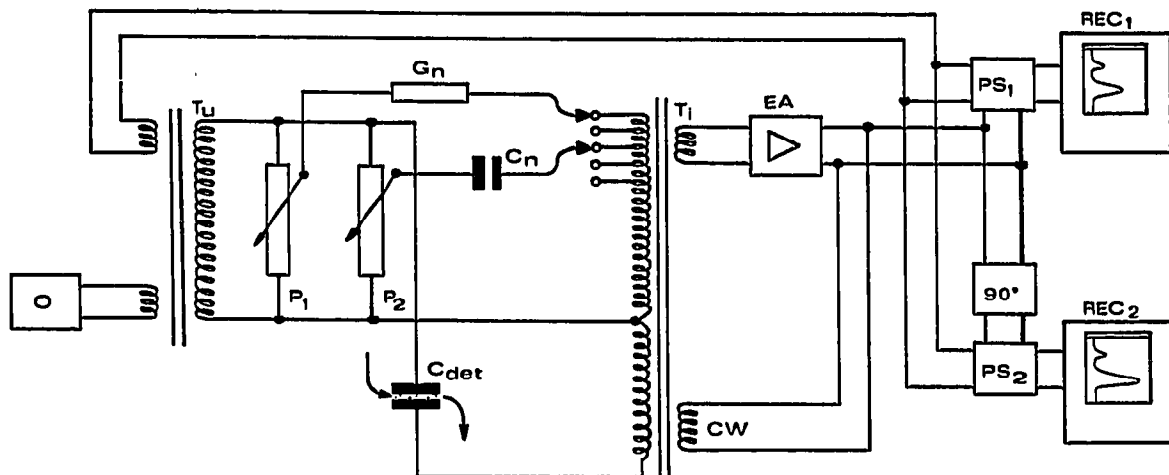
Fig. 5. Schematic diagram of self-balancing a.c. bridge detector.

different chemical compounds, but they are not sensitive enough to changes in concentration of binary mixtures in which the magnitude of the real components, ε'_{rx}, of the analyzed compound approaches that of the carrier, ε'_{rc}, and also in which the magnitude of the conductance component of the analyzed substance, $(g_x/\varepsilon_0 + \omega\varepsilon''_{rx})C_0$, is very small and approaches $(g_c/\varepsilon_0 + \omega\varepsilon''_{rc})C_0$ of a low-loss liquid carrier.

The amplitude of the oscillations in a resonant circuit is subject to change due to dissipation of energy from the circuit. As mentioned in the section on admittance detectors, a very high sensitivity to this effect may be attained in low-loss resonant circuits. It is necessary to suggest a detector based on this principle, but giving two separate signals, i.e., again for changes in $(g/\varepsilon_0 + \omega\varepsilon''_r)C_0$ and $\omega\varepsilon'_rC_0$ simultaneously. A new direct-reading resonance method was investigated from this point of view.

It has been shown[13] that the magnitude of the driving voltage, U_0, that is necessary in order to keep the magnitude of the resonance voltage, U_{cr}, constant at various losses and a constant frequency of a driving source, f_r, is a linear function of the conductance, G, connected in parallel with the capacitor of the circuit LCR_0 (Fig. 6). It holds for a conductance increment:

$$\Delta G = \frac{2\pi f_r C_r}{U_{cr}}\, \Delta U_0 = k \cdot \Delta U_0 \tag{30}$$

where

ΔG = increment of conductance parallel to the tuning capacitor C;
f_r = frequency of the driving source;
C_r = total capacitance in the resonance circuit at resonance;
U_{cr} = r.m.s. value of the voltage across the capacitor C at resonance;
ΔU_0 = r.m.s. value of the driving-voltage increment, necessary to keep U_{cr} constant, at values of G changed by ΔG;
k = proportionality constant.

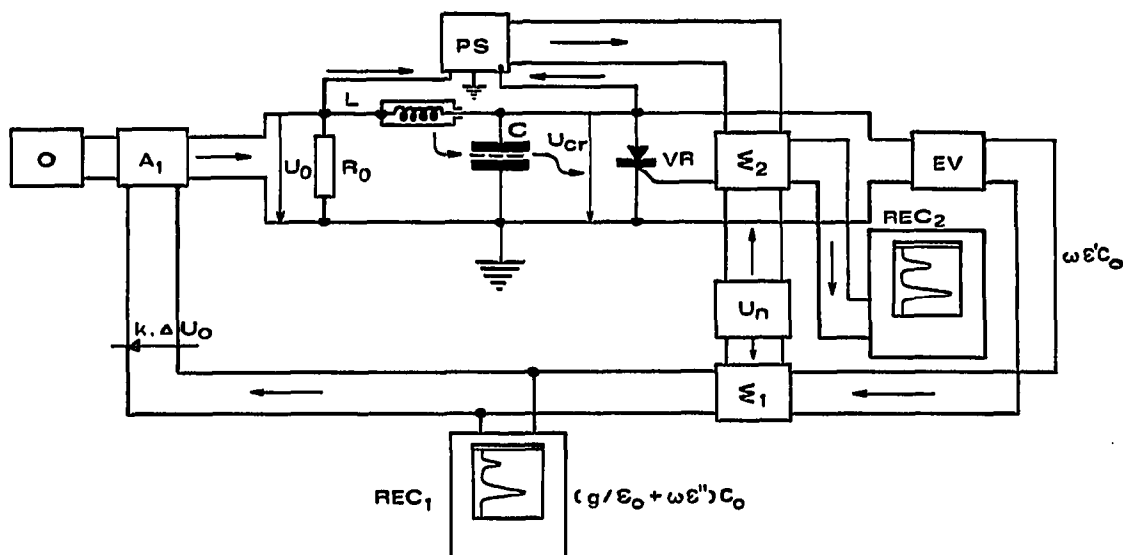The operating principle of the circuit can be explained by means of Fig. 6.

Fig. 6. Schematic diagram of self-balancing resonance detector.

The oscillator, O, drives a series resonant circuit, LCR_0, by a variable voltage, U_0, through a controlled-gain amplifier, A_1.

The resonant circuit, LCR_0, must be kept in resonance at the frequency f_r, on the one hand, and the driving voltage must be varied automatically in such a way that the voltage across the flow-through capacitor, C, remains constant. These two conditions must be fulfilled even if the conductance and the capacitance of the flow-through capacitor is changing. Thus, the circuit is tuned automatically to resonance by Varicap, VR, which obtains a control voltage from a phase-sensitive detector, PS, and a d.c. stabilized source, U_n. The phase-angle difference between U_0 and U_c is utilized as an error signal. In addition to the automatic tuning to resonance, the resonance voltage, U_{cr}, across the capacitor, C, is also kept constant by controlling the driving voltage, U_0, by means of a variable-gain electronic amplifier, A_1. The voltage difference between the rectified U_{cr} voltage and the adjustable voltage U_n is employed as an error signal for the control. The diode voltmeter, EV, and the comparator, Σ_1, are used for processing the U_{cr} voltage. The gain-control voltage, $k \cdot \Delta U_0$, and the Varicap control voltage are proportional to the conductance and capacitance increment due to the concentration of the substance being analyzed and are recorded by self-balancing recorders, REC_1 and REC_2.

The potentialities of this detector may be utilized particularly if solvents that have a very low loss tangent, tg δ, are used as carriers, especially organic solvents.

The system is suitable for use also at frequencies of the order of 10^8 Hz, where it enables the increased dielectric losses of some organic compounds to be utilized.

CONCLUSIONS

In these investigations of a new series of liquid chromatographic detectors, the dependence of electrical conductivity and of either of the components ε' and ε'' of

the complex permittivity on the concentration of a compound being analyzed present in a solvent used as the carrier liquid has been utilized. The flow-through capacitor was used as the detector sensor. Two kinds of capacitor design are recommended: a coaxial design for lumped-parameter circuits, and a flat circular design with coaxial and cavity resonators for frequencies of the order of 10^8 Hz. Various systems for the conversion of capacitor admittance increments into d.c. electrical signal have been critically reviewed, and two new automatic-balance systems of conversion are suggested, namely, a self-balancing capacitance detector and a self-balancing resonance detector.

It is believed that conductivity–permittivity detectors can contribute considerably to liquid chromatographic instrumentation.

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