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THE PROSPECTS OF SELECTIVE DETECTION BY CAPACITANCE DETECTORS IN LIQUID CHROMATOGRAPHY

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SUMMARY

Relationships have been derived theoretically for expressing the response of capacitance detectors for liquid chromatography to changes in solute concentration, for the real component of the complex permittivity as well as for the component associated with the change in the dielectric losses and conductivity of the binary mixture. A method is suggested which allows separate chromatograms corresponding to both above-mentioned components to be obtained.

INTRODUCTION

Until now, mainly the changes in the real component of complex permittivity, "dielectric constant", brought about by the presence of the detected substance in the carrier liquid, were considered in connection with capacitance detectors for liquid chromatography. A change of the real component ε' of the complex permittivity of a liquid results in a change of the capacity of the condenser through which the liquid is being passed. The capacity change in the detector, is converted to an electric signal suitable for a recorder input circuit. The recorder then provides a chromatogram whose instantaneous values are linear functions of the instantaneous values of the concentrations and of the differences between the real permittivity components of the detected substance and the carrier liquid.

However, the presence of the substance detected in the carrier liquid produces, besides a change in capacitance, a change in the conductance component G of the admittance Y of the measuring condenser as well, as the presence of the substance detected influences the dielectric losses, the latter having a linear relationship with the absolute value ε'' of the imaginary component of the complex permittivity, and the conductivity of the liquid dielectric, g.

The relationship between the magnitudes of the parameters ε', ε'', and g is characteristic for individual substances. The possibility of obtaining two separate chromatograms, of which one would be a linear function of the concentration m_x of the detected substance and of the real permittivity component of the latter, ε':

$$U_1 = f_1(m_x, \varepsilon_x') \tag{1}$$

and the other a linear function of the concentration m_x, conductivity g_x, and the absolute value of the imaginary component, ε_x'', of complex permittivity:

$$U_2 = f_2(m_x, g_x, \varepsilon_x'') \tag{2}$$

would represent a significant contribution to the identification of the substance under detection. The aim of the present paper is a theoretical analysis of the above problem.

THE RESPONSE OF CAPACITANCE DETECTORS

An approximately linear equation for the resultant real component ε_r' of a binary mixture in the range of low concentrations is given by

$$\varepsilon_r' = m_x \cdot \varepsilon_x' + (1 - m_x)\,\varepsilon_c' = m_x(\varepsilon_x' - \varepsilon_c') + \varepsilon_c' \tag{3}$$

Hence, the detected substance with the real component ε_x', present in a concentration m_x (expressed in volume fraction units), brings about a change of the real component ε' from the initial value ε_c', corresponding to pure carrier liquid, to ε_r':

$$\Delta\varepsilon' = \varepsilon_r' - \varepsilon_c' = m_x(\varepsilon_x' - \varepsilon_c') \tag{4}$$

A condenser filled with pure carrier liquid has a capacity:

$$C_c = \varepsilon_c' \cdot \varepsilon_0 \frac{S}{d} = \varepsilon_c'\, C_0 \tag{5}$$

and after filling it with the binary mixture,

$$C_r = \varepsilon_r'\, C_0 \tag{6}$$

Provided $\varepsilon_x' < \varepsilon_c'$, the following increment in the capacity occurs

$$\Delta C = C_r - C_c = (\varepsilon_r' - \varepsilon_c')\, C_0 = m_x(\varepsilon_x' - \varepsilon_c')\, C_0 \tag{7}$$

The capacity change is converted, by means of the measuring circuit in the detector, to an appropriate electrical signal which is recorded as a chromatogram,

$$U_1 = k_1 \cdot m_x(\varepsilon_x' - \varepsilon_c') \cdot C_0 \tag{8}$$

Eqn. 8 indicates that it is desirable, from the point of view of sensitivity, that the real component ε_x' of the substance detected should differ as much as possible from that of the permittivity of the carrier liquid, ε_c'.

The conversion of the capacity change to an electrical signal suitable for the recorder can be accomplished in various ways. Some of them have been described in the literature[1,2].

However, the presence of a component in the carrier liquid causes, along with a change in the capacity, a change in the conductance component of the admittance of the measuring condenser of the capacitance detector as well. We have found[2] that the equation below generally holds for the above component

$$G = (g + \omega \cdot \varepsilon'' \cdot \varepsilon_0)\, S/d \tag{9}$$

Rearranging this equation in another form we get:

$$G = \left(\frac{g}{\varepsilon_0} + \omega\varepsilon''\right)\cdot\varepsilon_0\cdot S/d = \left(\frac{g}{\varepsilon_0} + \omega\varepsilon''\right)\cdot C_0 \tag{10}$$

At low concentrations, it may be assumed for the resultant absolute value of the imaginary part of the complex permittivity of a binary mixture, analogously to eqn. 3, that:

$$\varepsilon_r'' = m_x\,\varepsilon_x'' + (1 - m_x)\,\varepsilon_c'' = m_x(\varepsilon_x'' - \varepsilon_c'') + \varepsilon_c'' \tag{11}$$

and for the increment

$$\Delta\varepsilon'' = m_x(\varepsilon_x'' - \varepsilon_c'') \tag{12}$$

The relationship between electrical conductivity and concentration has been the subject of many papers (conductometry). Let us introduce into our case the presupposition that this quantity also obeys a relationship analogous to eqns. 3 and 11. Then, provided the conductivity of the substance under detection is higher than that of the carrier ($g_x > g_c$), the conductivity increment is given by:

$$\Delta g = m_x(g_x - g_c) \tag{13}$$

The admittance of the condenser is generally given by:

$$\vec{Y} = G + jB = G + j\omega C \tag{14}$$

The resultant admittance increment may be determined from eqns. 7, 10, 12, 13 and 14:

$$\Delta\vec{Y} = m_x C_0\left[\frac{g_x - g_c}{\varepsilon_0} + \omega(\varepsilon_x'' - \varepsilon_c'') + j\omega(\varepsilon_x' - \varepsilon_c')\right] \tag{15}$$

The admittance increment may be converted, by means of an appropriate measuring circuit, to a change in voltage:

$$\Delta\vec{U} = K\,m_x C_0(\Delta G + j\Delta B) = \Delta\vec{U}_g + j\Delta\vec{U}_B \tag{16}$$

It may be inferred from the above equation that the increment in the admittance of the condenser through which the binary liquid mixture passes gives rise, in a linear measuring circuit, to a voltage composed of two components in quadrature, which are, within low concentration limits, linear functions of the concentration of the substance detected, expressed in volume fractions of the latter in the column effluent.

The systems for evaluating the changes of the admittance of the measuring capacitance detector may respond either to one of the components or to both components simultaneously.

Interference detectors[1], in which one of the oscillators previously tuned to a frequency equal to the other is detuned by the capacity change of the measuring condenser, and the difference in frequency is converted to a d.c. signal for the recorder, produce the required response to a change of the real component $\Delta\varepsilon'$ of the complex permittivity ε^* only. However, incidentally a higher rise in the conductance component of the admittance of the measuring condenser results in undesirable damping of the resonance circuit of the oscillator being detuned, which leads to the deterioration of the frequency stability and lowering of the amplitude of the oscillator vibrations. If the amplitude sinks below a certain limit, the mixer usually ceases to work and the detector fails.

The response of a detector in which the resonance principle[2] is employed for evaluating the changes in the admittance of the measuring condenser represents, at low concentrations, the sum of the responses to $\Delta\varepsilon'$ and $\Delta(g, \varepsilon'')$. This detector may also be used to detect substances to which the interference detectors do not react. These are such substances where the real components, ε_x', are equal to that of the carrier liquid, ε_c', but whose loss tangents, tg δ_x, are larger than tg δ_c of the carrier liquid. A further remarkable virtue of resonance detectors is their ability to detect the presence of substances with very low dielectric losses, to which other methods may be insensitive.

An important group of capacitance detectors is represented by systems in which use is made of an unbalanced a.c. bridge, derived from the Wheatstone d.c. bridge, for converting the changes of the admittance of the measuring condenser to the electric signal. The individual types of the above bridges differ from one another in that their arms are set up from a variety of combinations of basic elements: inductance coils L, condensers C, and resistors R, or, incidentally, mutual inductances M. In bridges used for detection in liquid chromatography, the measuring element is a condenser through which flows the liquid mixture under analysis. The bridge is balanced to give a zero reading when pure carrier liquid flows through the measuring condenser. It is advantageous to balance the bridge by means of a condenser since it is possible in this case to employ a reference condenser of the same construction, filled with the carrier liquid or through which the carrier liquid passes continuously[3]. From the point of view of design, it is of advantage if the measuring and the reference condensers are inserted in adjacent arms. In this case, both condensers may share a common electrode, which contributes substantially to the improvement of the temperature stability of the zero setting. However, the voltage across the diagonal of an unbalanced bridge of the Wheatstone type may only be used to obtain a single chromatogram, the voltage being a function of the concentration and of ε', ε'', g.

USE OF THE TRANSFORMER BRIDGE

The bridges derived from Wheatstone's principle operate by virtue of the comparison of potentials. The bridge is balanced if the a.c. potential at point A (Fig. 1) is equal both with respect to magnitude and phase to the potential at point B:

$$\vec{V}_{\mathrm{A}} = \vec{V}_{\mathrm{B}} \tag{17}$$

The bridge may have either the generator or the detector earthed. From the chromatographic point of view, it is advantageous if the measuring condenser of the detector can be placed in the immediate vicinity of the column, which requires the use of coaxial cables connecting the condenser with the bridge. The transversal admittances of the cables play a role when balancing the bridge, since the cables are

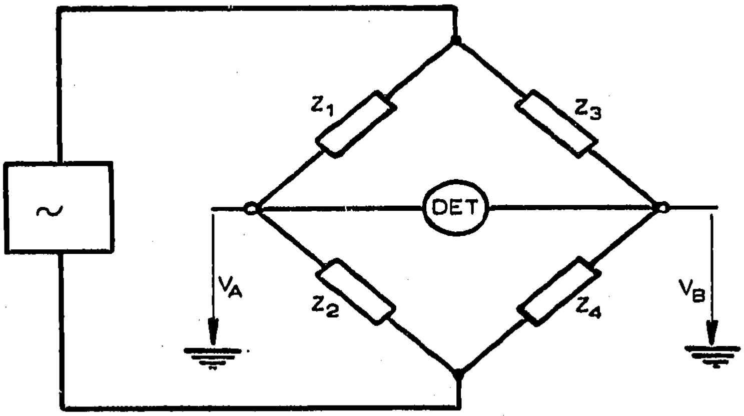

Fig. 1. Principle of balancing the bridges of the Wheatstone type.

situated parallel to the bridge branches and are connected to not insignificant potentials.

Transformer bridges[4-6], based on the comparison of the currents through the two impedances being compared, are remarkably suitable as permittivity detectors for liquid chromatography. The principle is illustrated in Fig. 2. A generator with a.c. voltage U_g supplies currents, I_n, I_x, through the impedances Z_n, Z_x being compared, into two electrically equal windings of the current transformer. The transformer is constructed very carefully with respect to attaining a very low leakage magnetic flux, so that the coupling coefficient κ of both windings approaches unity very closely:

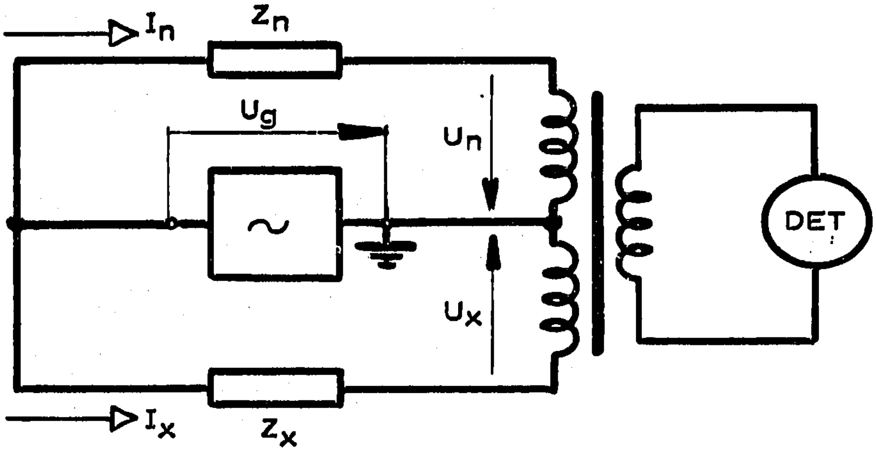

Fig. 2. Principle of the transformer bridge.

$$\kappa = M/\sqrt{L_{tn}L_{tx}} \doteq 1 \tag{18}$$

Provided both halves of the winding are electrically equal, $L_{tn} = L_{tx}$, $R_{tn} = R_{tx}$, the following holds very approximately:

$$L_{tn} = L_{tx} \doteq M \tag{19}$$

The voltages in the loops with impedances Z_n and Z_x are given by the Kirchhof equations:

$$\vec{U}_g = \vec{I}_n R_n + \vec{I}_n R_{tn} + j(X_n + \omega L_{tn})\,\vec{I}_n - j\omega M \vec{I}_x \tag{20}$$

$$\vec{U}_g = \vec{I}_x R_x + \vec{I}_x R_{tx} + j(X_x + \omega L_{tx})\,\vec{I}_x - j\omega M \vec{I}_n \tag{21}$$

Assuming the validity of eqn. 19, it must hold true for the balanced bridge that the currents in both branches are equal and that the magnetic fluxes in the core, incidental to the above currents, Φ_n, Φ_x, have equal absolute values and are mutually phase shifted by an angle of π, so that they are cancelled by each other. The voltages U_n and U_x are initiated by the voltage drop across the respective halves of the winding of the current transformer. As the coupling coefficient κ is very close to unity, very approximately:

$$j\omega L_{tn}\vec{I}_n - j\omega M \vec{I}_n = 0 \tag{22}$$

$$j\omega L_{tx}\vec{I}_x - j\omega M \vec{I}_n = 0 \tag{23}$$

so that the voltages U_n and U_x are produced only across the ohmic resistances of the windings:

$$\vec{U}_n = R_{tn}\vec{I}_n \doteq 0 \tag{24}$$

$$\vec{U}_x = R_{tx}\vec{I}_x \doteq 0 \tag{25}$$

Hence, the impedances Z_n and Z_x are at one terminal very approximately at a zero potential. This is of great importance for the operation of the detector, since Z_n and Z_x, as we shall see later, are the impedances of the reference and measuring condenser of the detector, and, as the impedances are practically earthed at one end, it is possible to connect this terminal of the detector condenser to the current transformer by coaxial cable of any arbitrary length without causing any deleterious effects on the performance of the detector.

On substituting the relations given by eqns. 22 and 23 into eqns. 20 and 21, while supposing the applicability of eqns. 24 and 25, one obtains for the currents I_n and I_x the relations:

$$\vec{I}_n = \vec{U}_g/\vec{Z}_n = \vec{U}_g\vec{Y}_n \tag{26}$$

$$\vec{I}_x = \vec{U}_g/\vec{Z}_x = \vec{U}_g\vec{Y}_x \tag{27}$$

i.e.

$$\frac{\vec{I}_x}{\vec{I}_n} = \frac{\vec{Z}_n}{\vec{Z}_x} = \frac{\vec{Y}_x}{\vec{Y}_n} \tag{28}$$

If the bridge is put out of balance, then

$$\vec{\Phi}_x \neq \vec{\Phi}_n \tag{29}$$

and there is induced a voltage in the third winding of the current transformer with the detector. The bridge may be balanced automatically by introducing a compensating magnetic flux by means of an auxiliary winding on the current transformer[6]. This winding is fed by the output current of an electronic amplifier having very high gain. As it is a requisite that the current in the third winding should approach zero, the input impedance of the amplifier must be very high.

The current in the compensating circuit has two components, an active in-phase component I_G and a reactive one, I_c, in quadrature, both being proportional to the respective increments of the components of the admittance of the measuring condenser of the detector, ΔG_x, and $\Delta \omega C_x$, as compared with the balanced state. If the output signal from the current transformer in a phase sensitive detector is compared with the in-phase component of the signal of the generator, a signal is obtained at the phase sensitive detector (PSD) output which is proportional to the change of the conductance component of the admittance of the measuring condenser. It follows from eqn. 15 that:

$$I_G = kUC_0 \left[\frac{g_x - g_c}{\varepsilon_0} + \omega(\varepsilon_x'' - \varepsilon_c'')\right] \cdot m_x \qquad (30)$$

In order to obtain a signal proportional to the capacity change due to the increase of ε', one of the signals must be rotated by an angle of 90° in a phase shifter. Analogously to eqn. 30, for this signal one obtains from eqn. 15:

$$I_c = kC_0U\omega(\varepsilon_x' - \varepsilon_c') \cdot m_x \qquad (31)$$

DEVELOPMENT OF THE DETECTOR

Bridges with inductivity coupled arms (transformer bridges) can be supplied by several manufacturers as universal bridges for measuring G and C within a very broad range of values. They are designed, on the one hand, for manual balancing, and, on the other hand, as autobalance bridges (Tesla, Wayne Kerr) which are coarsely balanced by manual switching over the tapped transformer; the fine balance is achieved automatically by a servo loop. The readout of the last two decimal places is carried out on the scale of a measuring instrument. In order to read G and C two separate instruments are employed. The analog signals for G and C may be employed for recording two separate chromatograms, if two slide-back recorders are connected in parallel with these instruments. A properly designed condenser, through which the mixture being chromatographed can be passed is placed at the column outlet, and is used as the detector sensor, which may be connected to the bridge by coaxial cables of any length.

Some brief information on the potentialities of selective detection by the above arrangement, is given by the following example where a Tesla BM 484 autobalance bridge (or Wayne Kerr B331) is used. Let us suppose that a condenser with the dimensions according to Fig. 3, having an internal volume of 10 μl, is used as the sensor. The capacity of the condenser cavity, with air, will be:

$$C_0 = \varepsilon_0 \frac{S}{d} = 35.37 \text{ pF}$$

Let us investigate what concentration, m_x, is required to produce a deflection

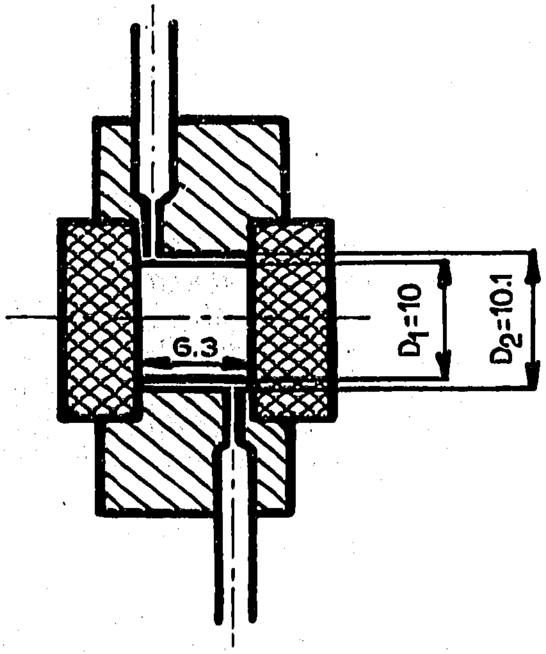

Fig. 3. Shape and dimensions of the measuring condenser.

ΔU of 1 mV, if carrier liquid with $\varepsilon_c' = 2$ is used and a substance with $\varepsilon_x' = 4$ is detected. To obtain an increment of 1 mV on the above-mentioned bridge, it is necessary to increase the capacity of the condenser by about 1:100,000 of the overall capacity, in our case:

$$\Delta C = \frac{70.74 \times 10^{-12}}{100{,}000} = 0.0007074 \text{ pF}$$

It follows from eqn. 7:

$$\Delta C = m_x(\varepsilon_x' - \varepsilon_c')\, C_0 = 0.0007074$$

and the required concentration, expressed in volume fraction, amounts to

$$m_x = \frac{0.0007074}{(4-2) \times 35.37} = 10^{-5}$$

The channel for the conductance component of the admittance has the same sensitivity as that for the capacitance component, so that a relationship may analogously be derived for the concentration m_x necessary for a voltage increment of 1 mV.

The sensitivity of detection attainable with the above bridge will obviously depend on the stability of the zero. If the stability of the zero permits the connection of recorders with a sensitivity of 1 mV f.s.d. in parallel with the measuring instruments for G and C, chromatograms with sufficiently high peaks may be obtained for concentrations lower by one order of magnitude than m_x above *i.e.* for units of 10^{-6}.

A SINGLE-PURPOSE BRIDGE FOR THE DETECTOR

The use of a universal autobalance transformer bridge offers remarkable

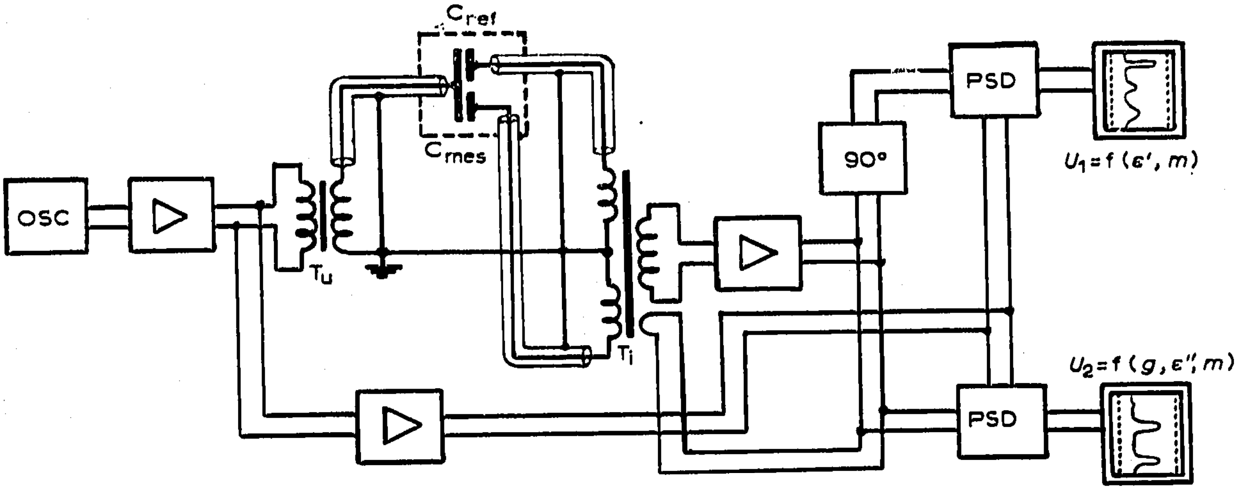

Fig. 4. Circuit diagram of the selective detector: C_{ref}, C_{mes} = dual condenser; T_u = voltage transformer; T_i = current transformer; PSD = phase sensitive detectors.

possibilities of selective detection in liquid chromatography. However, the universal bridge was designed specifically for measuring G and C and, possibly L, within wide limits. For detection in liquid chromatography, the problem is to obtain a signal whose instantaneous value is a linear function of the instantaneous solute concentration, rather than the measurement of the components of the condenser admittance. From this point of view, many of the possibilities offered by the universal bridge remains unexploited. On the other hand, it is desirable that the device should show the highest possible sensitivity to changes in the solute concentration, the zero line being insensitive to variations in room temperature, fluctuations of the mains, etc. and these requirements may be met much better by a single-purpose bridge.

In the universal bridge, the measuring condenser is connected into one current branch, and the components of the condenser admittance, G_x, ωC_x, are backed off by the components of the admittance of a variable capacity standard, G_n, ωC_n, in the reference branch. A change of the carrier liquid brings about a change in the admittance of the measuring condenser, and the admittance of the standard in the reference branch must be set to a new value, corresponding to the parameters ε_c', ε_c'', and g_c of the new carrier liquid. This procedure may be eliminated by the detector illustrated in Fig. 4. Instead of the variable capacity standard, a reference condenser of the same construction as the measuring one is used in this case, either filled with pure carrier liquid or through which pure carrier liquid flows. Slight differences in the admittance of the reference and the measuring branches can be compensated by the capacity and resistance trimmers. Now, if a different carrier liquid is used, the same change occurs in both branches, and a single value of the reference condenser is sufficient. If both condensers, the reference and the measuring one, having a common electrode, are located in the same metal block, a considerable independence of the zero line of the variations in the room temperature is attained.

In the bridge designed especially for the purpose of selective detection, the sensitivity may also be enhanced by raising the voltage across the measuring and the reference condensers, as compared to the respective values usual in universal auto-balance bridges where the product is intended for the measurement over a wide measuring range. An increase in the stability of the generator voltage and of the gain of the error voltage amplifier may also contribute essentially to the enhancement of the detector sensitivity to concentration changes.

CONCLUSIONS

A change in both components of the admittance of the measuring condensor in a capacitance detector for liquid chromatography is approximately a linear function of the solute concentration expressed by the volume fraction. As the relationship between the conductance and the susceptance components of the above admittance is characteristic for a given component of the liquid mixture chromatographed, the separate recording of the chromatograms of both admittance components offers the possibility of selective detection.

In order to obtain the separate signals for both chromatograms, it is necessary to resolve the electric current in the measuring condenser to the component in phase with the voltage across the condenser and the component in quadrature, which may be achieved by means of two phase-sensitive detectors and a 90° phase shifter.

For selective detection by the above method, autobalance transformer bridges may be employed which allow the measuring condenser to be connected to the bridge terminals by coaxial cables of any practical length. This is especially advantageous if the measuring condenser must be placed in a thermostat.

A special-purpose transformer bridge designed so as to enable the use of a dual condenser is noteworthy. With this variant, one may expect the base line to be practically independent of the fluctuations in the room temperature and that of carrier liquid. The use of higher measuring frequencies allows condensers to be employed which have lower capacities, and, therefore, have smaller volumes.

LIST OF THE SYMBOLS

C_0	Capacity of the measuring condenser with air dielectric
C_c, C_r	Capacity of the measuring condenser with pure carrier liquid, and with the resultant mixture, respectively
g_c, g_r, g_x	Conductivity of the pure carrier, resultant binary mixture, and detected component, respectively
G	Conductance of the measuring condenser
I_n, I_x	Currents in the reference and the measuring condensers, respectively
j	Imaginary unit ($j^2 = -1$)
k, K	Proportionality factors
L_{tn}, L_{tx}	Inductivity of the transformer windings of the reference and the measuring branches
m_x	Concentration of the component under detection in the carrier liquid, in volume fraction
M	Mutual inductivity of the current transformer windings
R_n, R_x	Resistance of the reference and the measured impedances
U_g	Generator voltage
V_A, V_B	Potential at the points A and B, respectively
X_n, X_x	Reactance of the reference and the measured impedances

Y_n, Y_x	Admittance of the reference and measuring condensers
Z_n, Z_x	Impedance of the reference and measuring condensers
ε^*	Complex permittivity
ε'	Real component of the complex permittivity
ε''	Absolute value of the imaginary component of the complex permittivity
ε_0	Permittivity of the free space angular frequency (ω of the internal generator $= 10^4$ in BM 484 and B 331 bridges, *i.e.* $f = 1{,}592$ Hz)

Subscripts c, r, and x correspond to the carrier, resultant mixture, and the detected component, respectively.

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