THEORY OF CONCENTRATION DETERMINATION BY HIGH FREQUENCIES

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The concentration determination by high frequencies is a new method of conductometric measurements. The principle of the measuring and the description of the high frequency titration apparatus can be found in several articles [2, 3, 4], BLAEDEL, MALMSTADT and others discuss the semi-quantitative theory of the method [5, 6, 7, 8, 9], while REILLEY and McCURDY deal with the question of optimum measuring point [8].

The high-frequency concentration determination is based on the following phenomena : if one makes a coupling between the tank circuit of a vacuum tube oscillator and the material to be examined, then both the frequency and the amplitude of the voltage generated by the oscillator changes, the change being in close connection with the conductivity and the dielectric constant of the material to be examined. In case of aqueous solutions the dielectric constant can be regarded approximatively as constant, so the change of frequency or amplitude depends on the conductivity and, consequently, on the concentration. A special feature of the method is that there is no need for direct contacts between the tank circuit and the substance to be investigated, the measuring electrodes can be placed on the outside of the container, or in the case of measurements made inside the coil they can simply be omitted. This is possible because there the capacitive coupling through the glass wall is enough at high frequencies.

I. The measuring method

The measuring is carried out in an electric tuned circuit. It contains an inductance, capacitance and — mainly because of the ohmic loss of the coil — a resistance. The reciprocal of the a. c. resistance of the circuit, the admittance is :

$$Y = G + j\,\omega\,C + \frac{1}{j\,\omega\,L}$$

where G is the reciprocal of the loss resistance

L the inductivity of the circuit

C the capacity of the circuit

ω the frequency f multiplied by 2π $(\omega = 2\pi f)$

j the imaginary unit $j = \sqrt{-1}$.

Since G can be regarded independent of frequency, the admittance is minimal if we make the imaginar part of the admittance zero

$$j\omega C + \frac{1}{j\omega L} = 0\,.$$

From this, the well-known Thomson formula gives the resonant frequency of the circuit :

$$\omega_0^2 = \frac{1}{LC}\,.$$

By derivating the Thomson formula, one can determine the change of resonant frequency, due to small capacity variation

$$\frac{\Delta\omega}{\omega_0} = \frac{\Delta f}{f_0} = -\frac{1}{2}\frac{\Delta C}{C}.$$

The admittance of the tuned circuit decreases at resonant frequency to a value equal to that of the reciprocal of the loss resistance and becomes ohmic. This can be explained physically by the fact that the electrical energy which is accumulated during one half cycle changes over to magnetic energy during the next half cycle in the magnetic field of the coil, and this energy oscillates between the electric field of the capacitance and the magnetic field of the coil. From the outside only small energy is required to compensate for the losses.

The oscillating electro-magnetic energy is much greater than the loss which becomes Joule heat, the ratio of the two energies is the quality factor of the tuned circuit.

The substance to be measured can be placed, either in the capacitor, or within the coil. When measuring within the coil the stray capacity of the coil serves as the measuring capacitance, the effect of eddy currents — according to our theoretical calculations — can be neglected. A great number of our experiments proved this. In the following discussion we deal with the flat-plate measuring capacitor. We note, however, that either the cylindrical measuring capacitor or the coil are equivalent to a properly chosen flat-plate capacitor.

II. Flat-plate measuring capacitance

In case of flat-plate measuring capacitance, the liquid to be examined is placed in a glass container having plane sides. The electrodes of the capacitance are on the outside of the glass container. The surface area of the flat-plate measuring capacitance on Fig. 1 is F, the thickness of the glass wall a,
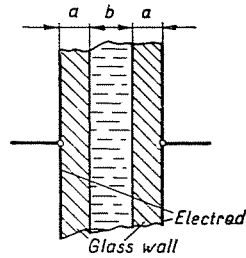
Fig. 1. Measuring capacitance with plane electrodes

the thickness of the liquid is b. The potential at the interface between the glass walls and the liquid is the same throughout, so if we place a very thin metal plate at both surfaces, there will be no disturbance of the field. This arrangement — which is electrically equivalent to the original measuring capacitance — is shown in Fig. 2a. In Fig. 2b we divided the measuring capacitance into three capacitances in series, then on Fig. 2c the two outside capacitances, which
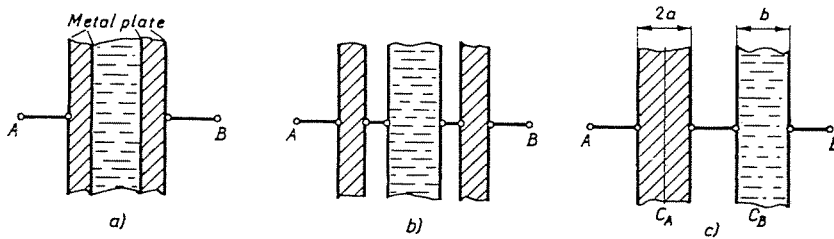

Fig. 2. Substituted pictures of flatplate measuring capacitance

are electrically equal, have been united into one with a dielectric layer of double thickness.

In the above discussion the flat-plate measuring capacitance has been reduced to the series combination of C_A and C_B. The electrical characters of this system can be determined in the following conditions :

a) The dimensions of the electrodes are much greater, than the distance between them.

b) The wall of the glass container is quite homogeneous, its thickness s a, its dielectric constant is ε_2 and can be regarded loss-free, that is :

$$\varkappa_2 = 0.$$

c) The liquid is homogeneous, its dielectric constant is ε_1, its conductivity $\varkappa_1$.

d) The electrodes of the capacitance receive a sinusoidal voltage.
Fig. 3 shows the electrical equivalent of the C_B capacitance, the dielectric of which is the liquid associated with loss.
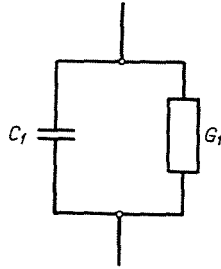
Fig. 3. Electrical equivalent of capacitance filled with lossy dielectric

Assuming the MKS measuring system, the C_1 capacitive component result-
ing from the dielectric characters of the liquid, is

$$C_1 = \varepsilon_1 \cdot \varepsilon_0 \frac{F}{b} \,,$$

where ε_0 is the dielectric constant of the vacuum. The conductance G_1, as the
effect of conductivity

$$G_1 = \varkappa_1 \frac{F}{b}.$$

The admittance of the C_B capacitance filled with lossy dielectric is

$$Y_1 = j\,\omega\,C_B = G_1 + j\,\omega\,C_1 = \varkappa_1 \frac{F}{b} + j\,\omega\,\varepsilon_1\,\varepsilon_0\,\frac{F}{b} = j\,\omega\,\varepsilon_1\left(1 - j\,\frac{\varkappa_1}{\omega\,\varepsilon_0\,\varepsilon_1}\right)\varepsilon_0\,\frac{F}{b}\,.$$

This can be assumed as a capacitance which has the capacity in vacuum

$$C_0 = \varepsilon_0 \frac{F}{b},$$

the dielectric constant of the dielectric in it is the so-called complex-dielectric
constant :

$$\bar{\varepsilon} = \varepsilon_1\left(1 - j\,\frac{\varkappa}{\omega\,\varepsilon_0\,\varepsilon_1}\right) = \varepsilon_1\,(1 - jd)$$

where

$$d = \frac{\varkappa}{\omega\,\varepsilon_0\,\varepsilon_1}$$
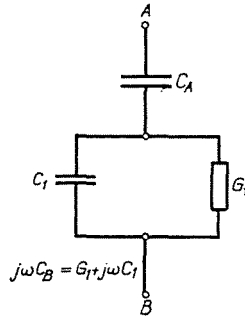
is the loss-factor.

Fig. 4. Substituted picture of measuring capacitance

According to this, the admittance between points A and B is — with the symbol

$$a = \frac{C_0}{C_A}$$

and Fig. 4 (which shows the relation between C_A and C_B) —

$$Y_{AB} = j\,\omega\,\frac{C_A C_B}{C_A + C_B} = j\,\omega\,C_A\,\frac{a\cdot\varepsilon_1(1 - j\,d)}{1 + a\,\varepsilon_1(1 - j\,d)}\,.$$

The imaginary part of this is the capacitive component :

$$\omega\,C_{AB} = \mathcal{Im}\,Y_{AB} = \omega\,C_A\,\frac{(a\,\varepsilon_1\,d)^2 + (a\,\varepsilon_1)^2}{(1 + a\,\varepsilon_1)^2 + (a\,\varepsilon_1\,d)^2}\,.$$

While the real part is the ohmic component associated with loss

$$G_{AB} = \mathcal{Re}\,Y_{AB} = \omega\,C_A\,\frac{a\,\varepsilon_1\,d}{(1 + a\,\varepsilon_1)^2 + (a\,\varepsilon_1\,d)^2}\,.$$

In case of cylindrical measuring capacitance, or in case of measurements made inside the coil, similar relations can be calculated. It is more suitable, however, to determine the values of a and C_A experimentally.

III. Examination of insulating liquids

In case of insulating liquids, the conductivity together with the value d can be regarded as zero. On account of this, there will be no loss component, that is :

$$d = 0.$$

The capacitive component depends on the dielectric constant of the liquid

$$C_{AB} = C_A\,\frac{a\,\varepsilon_1}{1 + a\,\varepsilon_1}\,.$$
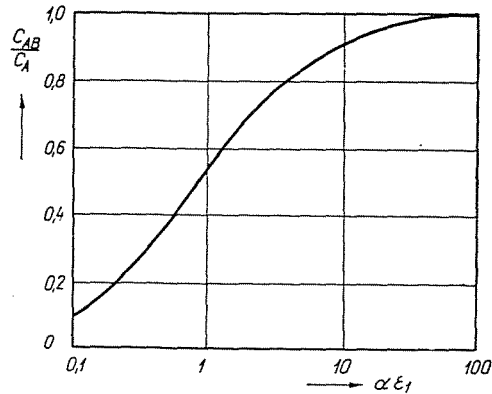
Fig. 5. Relative capacity of measuring capacitance

In Fig. 5 is shown the ratio of C_{AB}/C_A plotted against the parameter $\alpha \varepsilon_1$. The results of our measurements made on insulating liquids of different dielectric constants are shown in Fig. 6.
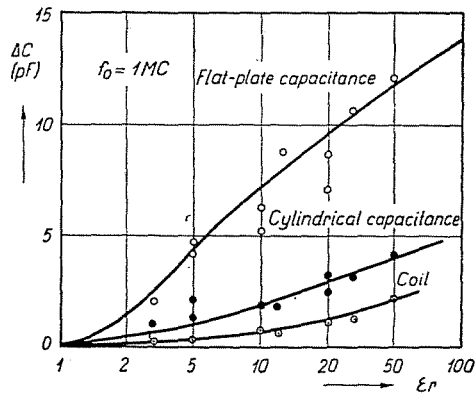

Fig. 6. Measurements made on insulating liquids

IV. Examination of electrolytes

In case of electrolytes we first examine a special case, when the conductivity can be regarded as zero (distilled water). In this case

$$d \to 0$$

so in case of a measuring container filled with distilled water, the capacitive component is

$$C_{AB}^{(water)} = C_W = C_A \left(\frac{\alpha \varepsilon_1}{1 + \alpha \varepsilon_1} \right)^2 = C_A \, \Phi^2.$$

Using this result, the relative changes in container capacity in respect to that of the distilled water's one are

$$\frac{\Delta C}{C_W} = \frac{C_{AB} - C_W}{C_W} = (1 - \Phi^2)\,\frac{\Phi^2 d^2}{1 + \Phi^2 d^2}$$

and

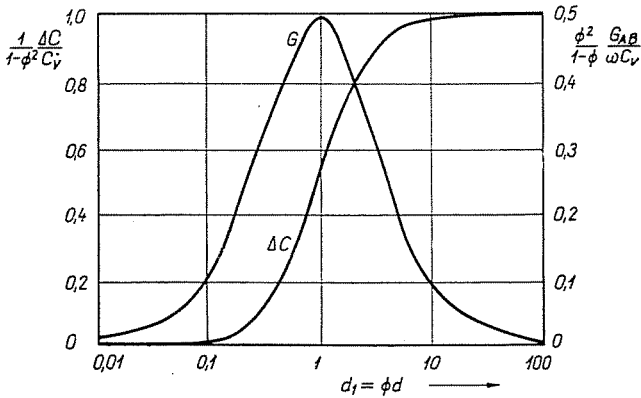$$\frac{C_1}{\omega\,C_W} = \frac{1 - \Phi}{\Phi^2} \cdot \frac{\Phi d}{1 + \Phi^2 d^2}.$$

Fig. 7. Characteristic curves in case of electrolytes

The above relations are shown in Fig. 7 using the symbol

$$\Phi = \frac{a\,\varepsilon_1}{1 + a\,\varepsilon_1}.$$

Fig. 8 shows the results of measurements made by the authors at a frequency of 10 MC/s with different types of measuring capacitances.
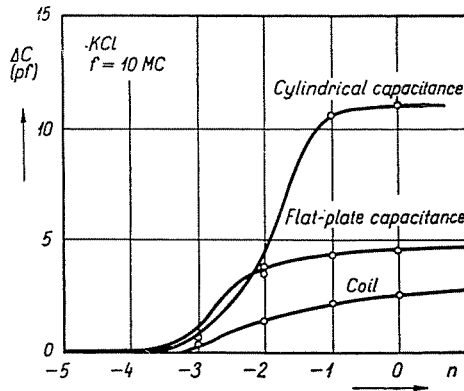

Fig. 8. Change of capacity for measuring capacitances filled with KCl plotted against concentration

V. Optimum measuring conditions

It was shown in the preceeding discussion that the change of capacity and loss resistance — which in turn are caused by the change of concentration and conductivity — are functions of the quantity d_1. Since d_1 depends on the geometry of the measuring cell, on frequency and on conductivity, optimum measuring conditions can be set up only if there exists a proper relation among these three quantities.

It was established that

$$d_1 = \Phi \cdot d$$

and

$$d = \frac{\varkappa}{\omega \, \varepsilon_0 \, \varepsilon_1}$$

therefore at a given measuring apparatus — where Φ stands for the geometrical dimensions — the resulting change is the function of

$$\frac{\varkappa}{\omega} = \frac{\varkappa}{2 \, \pi f},$$

that is, at a cell of given dimensions the measuring conditions can be regarded as unchanged if the ratio of the measuring frequency and the specific conductivity remains constant. Consequently, in the case of high concentrations it is better to measure at high frequencies, while in the case of low concentration lower frequencies are more useful.

In the case of measuring capacitance with plane electrodes the value of Φ plotted against the values of different a/b ratios is shown in Fig. 9.
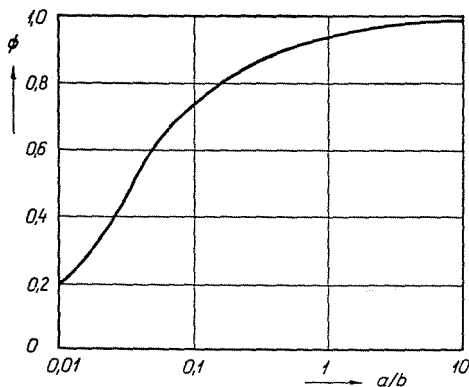

Fig. 9. Φ constant of measuring capacitance with plane electrodes

In this we used the marking of Fig. 1

$$\alpha = \frac{2 \, a}{\varepsilon_2 \, b}$$

and a glass of the dielectric constant $\varepsilon_2 = 6$, and water of the dielectric constant $\varepsilon_1 = 80$ were considered.

From the logarithmic derivates of the relations corresponding to the change of capacity and loss-conductance one can determine the optimum measuring point around which the change of concentration causes the greatest change in electrical properties. This is due to the maximum of the first derivative,
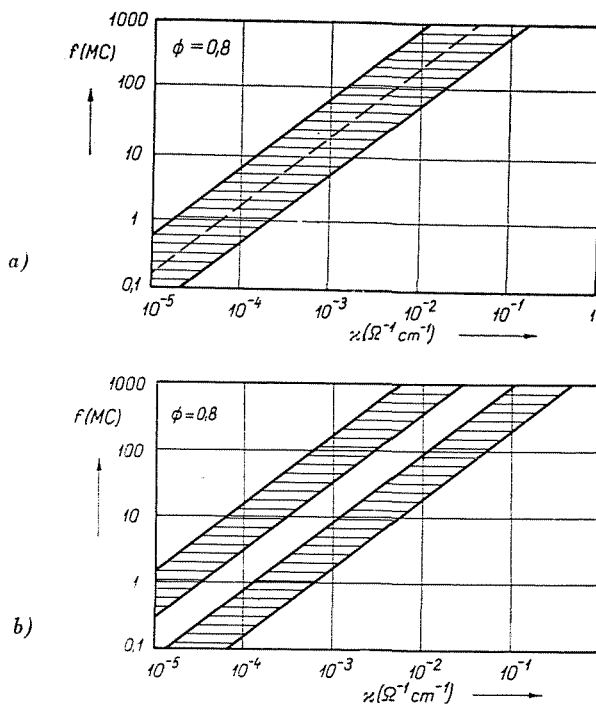

Fig. 10. a) Measuring limits in case of capacity measuring. b) Measuring limits in case of resistance measuring

that is where the second derivative is zero, therefore at the point of inflexion of the original curve. Another advantage of measuring near to the point of inflexion is that the relations between the change of concentration and the electrical quantities are linear.

When measuring the capacity change, the sensitivity is the greatest at

$$d_1 = 1.$$

Still, proper sensitivity can be reached between the values

$$d_1 = 0{,}33 \quad \text{and} \quad d_1 = 3$$

of the concentration range (Fig. 10a).

The measurement of loss resistance secures the optimum sensitivity around the points :

$$d_1 = \sqrt{3 \pm 2\sqrt{2}} = \begin{cases} 0{,}415 \\ 2{,}31 \end{cases}$$

When measuring near the first point of inflexion ($d_1 = 0{,}415$), the best results can be reached between the concentration range corresponding to the values of

$$d_1 = 0{,}1 \text{ and } d_1 = 0{,}5$$

and around the second point of inflexion it is advisable to measure between

$$d_1 = 2 \text{ and } d_1 = 9{,}9$$

to obtain a univocal and sensitive measurement (Fig. 10b).

It is advantageous to choose the geometry of the measuring container and the frequency according to the optimum value of d_1.

The best frequency for measurement in this case is :

$$f = 2{,}25 \cdot 10^4 \cdot \Phi \frac{\varkappa\left[\frac{1}{\Omega\,\mathrm{cm}}\right]}{d_{1\mathrm{opt}}} \; [MC/s]$$

Acknowledgements

Summary

The paper discusses the theoretical basis of the high frequency measuring method and the possibilities for its optimum set-up.

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