26. **Yuichi Kamura**: High Frequency Titrations. XIII.1) Studies on Concentration Curve by Capacitance-type Instrument.

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In high frequency titrations, various workers have pointed out the fact that the sensitivity is influenced by concentrations of a test solution, the typical case of this fact being shown in Fig. 1. With the addition of hydrochloric acid into water, the sensitivity drops smoothly showing a minimum at a certain concentration of hydrochloric acid. This fact proved a disadvantage for the use of high frequency titrations in that the restriction does exist for choosing suitable concentrations under which titrations should be carried out.

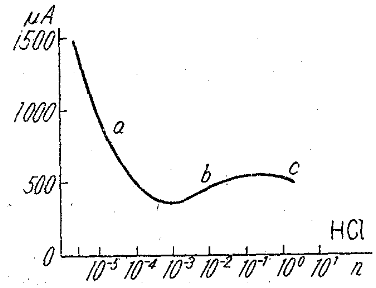

Fig. 1.
Concentration Curve (by condenser)

Although various works2~4) have been made to interprete the shape of concentration curves, definite explanation has still remained unsolved. In many cases, the attention has centered in clarifying only a part of the concentration. In the present report, an attempt is given for the comprehensive clarification for the shape of concentration curves.

In the theory appearing so far, the following problems should be considered:

1) Since an oscillator has many non-linear factors, the use of an oscillator is not suitable for the theoretical interpretation.

2) A comprehensive clarification for the concentration curve cannot be given by detailed studies on a particular part of a whole circuit, such as the electrodes.

3) Doubt exists as to the derivation of formulae.

An equivalent circuit of electrodes was converted into parallel form and the change in each R and C was followed. The calculated results only agreed with the experimental results when the parallel circuit was used. In general cases of high frequency instruments, the change is given as a total impedance which should be a sum of vectors C and R, and, moreover, the tuned phenomena must be taken into consideration. Even if the calculated results of parallel form showed a good agreement to the measured results in which the change in R and C is followed by a bridge in parallel circuit, it should be safe that the whole clarification is not given for the concentration curve of a tuned plate-tuned grid5~6) or a heterodyne-type7~8) instrument. In the latter case, the frequency changes not only by C but also by R.

The attempt which is discussed in the present paper is as follows:

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* Hongo, Tokyo (嘉村祐一).
1) Part XII: J. Pharm. Soc. Japan, **75**, 260(1955).
2) W. J. Bleadel, H. V. Malmstadt: Anal. Chem., **22**, 734(1950).
3) W. J. Bleadel: *Ibid.*, **24**, 198(1952).
4) C. N. Reilley, W. H. McCurdy: *Ibid.*, **25**, 36(1953).
5) F. W. Jensen, A. L. Parrack: Ind. Eng. Chem., Anal. Ed., **13**, 595(1946).
6) M. Ishibashi, T. Fujinaga, Y. Mitamure: Japan Analyst, **3**, 195(1953).
7) P. W. West, T. S. Burkhaltor, L. Broussard: Anal. Chem., **22**, 469(1950).
8) W. J. Bleadel, H. V. Malmstadt: *Ibid.*, **22**, 1413(1950).

1) All the factors which can be considered in a given circuit, including electrodes, are taken into calculation. Particularly L gives a great effect.

2) In order to avoid factors which cause a non-linear characteristics such as by a vacuum tube, the receiving-type titrimeter[9] in which each component is clearly defined was chosen (see Fig. 2).

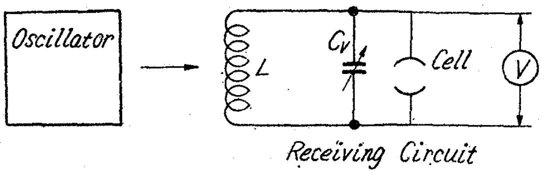


Fig. 2.
Receiving-type Titrimeter

In this type of instrument, the fact that L- and C-tuned circuit is independent of the oscillator permits the supply of a constant frequency and power, being almost independent of the change in concentration. The change in L and C circuit can be calculated and measured as a decrease in voltage, V. For the actual calculation, two parts are mentioned.

A) Preliminary experiment

In order to demonstrate the fact that the curve is influenced by the way of measurement and the suitability of the assumed equivalent circuit of the electrodes, the following means are taken :

As in the case of conductometric titration of a low frequency, the electrodes are immersed in a solution with the supply of high frequency electricity. Both by experiment and calculation, the studies are made for establishing a suitable equivalent circuit and for a characteristic response. This method is called a "direct method."

Second method represents a general case of high frequency titration. The change in solution is followed through the insulator, the beaker. The same studies as in the first case are made. This is called an "indirect method."

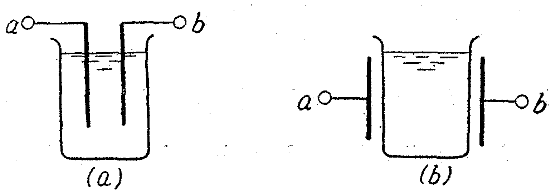
B) Concentration curve

By using equivalent circuit which was established in the preliminary experiment, the calculation is made for the series-tuned circuit. The concentration curve is obtained as a decrease in voltage, which is plotted on a curve showing points, a, b, and c in Fig. 1.

Experimental

I. Fundamental

A) **Direct measurement**—The equivalent circuit of Fig. 3a is replaced as is shown in Fig. 5, then is converted into series and parallel forms, the change in each C and R being determined. The changes in C and R measured by the bridge in Fig. 4 show a good agreement with those calculated, indicating the suitability of the equivalent circuit. The curve shows a peak of loss in a series form, while no peak in parallel. It is interesting that different method in measurement causes such remarkable difference for the same object. In Fig. 5, R_1=resistance, in series to the electrode, R_2=resistance in solution, C_0=electric capacity, and e=dielectric constant of a solution.



(a) direct (b) in direct

Fig. 3.
Cell

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[9] Y. Kamura : J. Japan. Chem., **6**, 771 (1952).

Fig. 4.

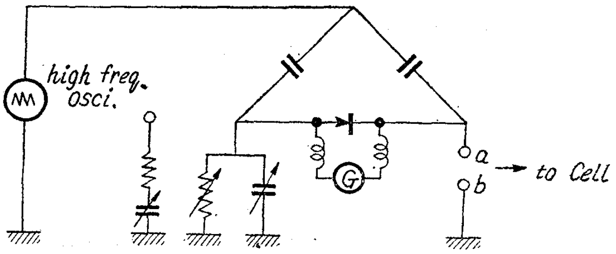
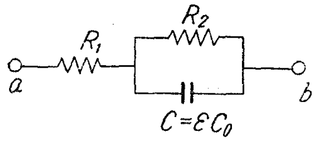


Fig. 5.
Equivalent circuit
of Fig. 3a



If Z is the impedance between a and b,

$$Z=\frac{(R_1+R_2)+j\omega CR_1R_2}{1+j\omega CR_2}\cdots\cdots(1)$$

1) Series method:

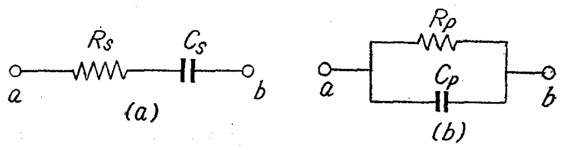
Equation (1) is put in the series of Fig. 6a to obtain R_s and C_s, where

$$R_s=\frac{R_1+R_2+\omega^2C^2R_1R_2{}^2}{1+\omega^2C^2R_2{}^2}\cdots\cdots(2)$$

$$C_s=\frac{1+\omega^2C^2R_2{}^2}{\omega^2C^2R_2{}^2}C\cdots\cdots(3)$$

Set $R=f\left(\frac{1}{\omega C}\right)$

Fig. 6.



The theoretical curve for the change in (2) and (3) is shown in Fig. 7a.

Fig. 7a.
Theoretical Curve of Series (direct)

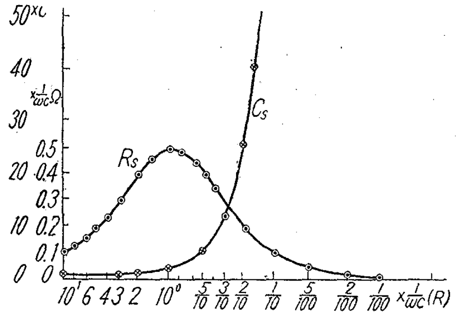
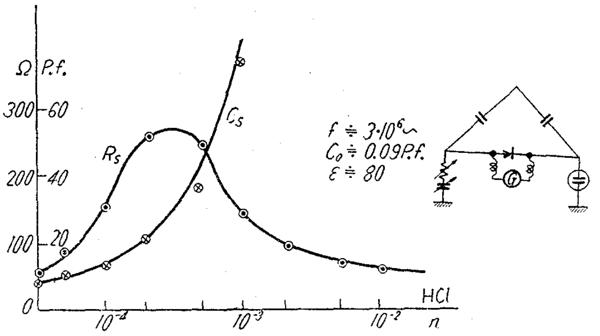


Fig. 7b.
Experimental Curve of Series (direct)



The frequency of platinum electrodes is $f\doteqdot3$ m.c. for the dimension of measurable specific resistance.

$$\frac{1}{\omega C}\doteqdot8.3\times10^{-3}\Omega\cdots\cdots(4)$$

(Dielectric constant of solution. Capacity of the electrides $C_0=0.09$ p.f., $C=7.2$ p.f. the loss reaches maximum at the point where $R=\frac{1}{\omega C}$ showing a good agreement with the results obtained by Forman and Crisp[10] and by the direct measurement, with the fact that C_2 increases remarkably towards ∞ with the decrease in R. The observed curve is shown in Fig. 7b.

The resistance of low frequency at the maximum of loss is

$$R\doteqdot9\times10^3\Omega$$

This value is in good agreement with the theoretical value (4) showing the same tendency in C_s.

2) Parallel method:

As is shown in Fig. 6, the curve in parallel form is quite different, showing no minimum and maximum in the loss.

$$R_p=\frac{(R_1+R_2)^2+\omega^2C^2R_1{}^2R_2{}^2}{R_1+R_2+\omega^2C^2R_1R_2{}^2}\cdots\cdots(6)$$

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[10] J. Forman, T. Crisp: Trans. Faraday Soc., **42** A, 186(1946).

$$C_p = \frac{R_2^2}{(R_1+R_2)^2+\omega^2C^2R_1^2R_2^2}C \quad \cdots\cdots(7)$$

Similar to the series method, both theoretical and observed values are shown in Figs. 8a and 8b.

Fig. 8a.
Theoretical Curve of Parallel (direct)

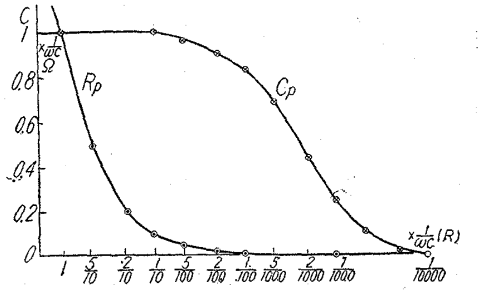
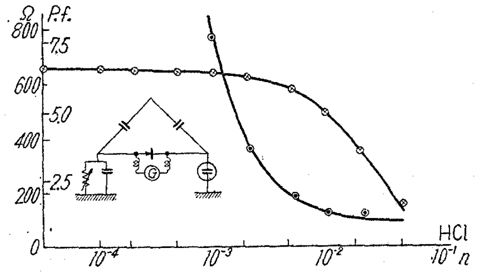


Fig. 8b.
Experimental* Curve of Parallel (direct)



$$R_1 = \frac{1}{10^3}\,\frac{1}{\omega C}$$

From the above calculations and measurement, the following conclusion should be drawn:

1) The equivalent circuit of Fig. 5 is acceptable.

2) The factor causing a peak is not only due to the electrode, but also the method of measurement must be taken into consideration.

B) Indirect measurement—By the method which was established by the direct measurement, the factor of which can be defined quite clearly, the assumption of an equivalent circuit is made (Fig. 9).

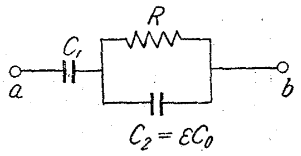


Fig. 9.

This equivalent circuit has been used by many workers[3] and very common. The series and parallel forms[4] of this equivalent circuit are mentioned below.

1) Series method:

$$R_s = \frac{R}{\omega^2C_1^2R^2+1} \quad \cdots\cdots(8)$$

$$C_s = \frac{\omega^2C_2^2R^2+1}{\omega^2C_2(C_1+C_2)R^2+1}C_1 \quad \cdots\cdots(9)$$

$$\text{Set} \quad R = f\left(\frac{1}{\omega C}\right)$$

Fig. 10a.
Theoretical Curve of Series (indirect)

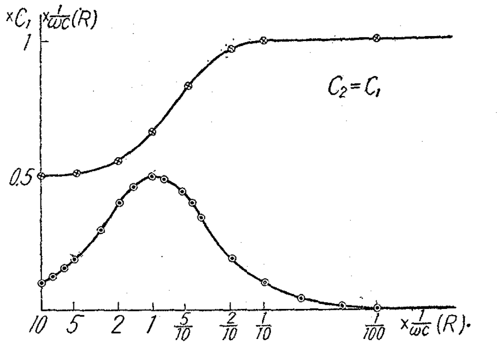
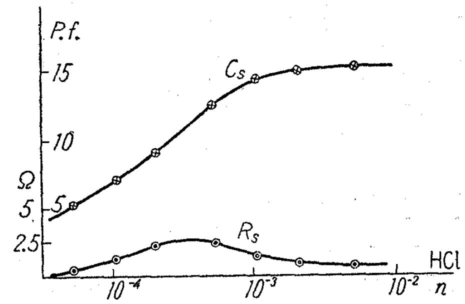


Fig. 10b.
Experimental Curve of Series (indirect)



The theoretical and measured curves are shown in Figs. 10a and 10b. Both curves show similarity (even if the specific resistance can be obtained, the quantitative comparison can hardly be made because of the difficulty of measuring R).

2) Parallel method:

The theoretical and observed curves are shown in Figs. 11a and 11b. The following conclusion can be drawn by comparing these results of both direct and indirect methods.

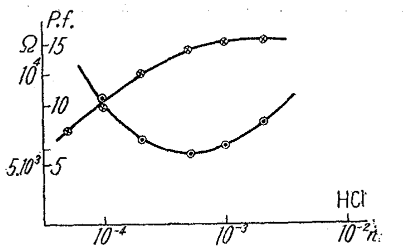
1) The equivalent circuit of electrodes is acceptable for practical use.

2) The difference can be observed between the curves by the series and parallel methods.

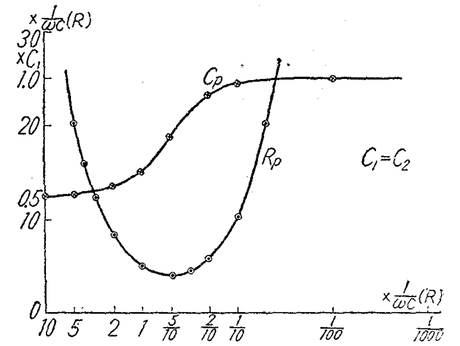
Although this difference is not remarkable in comparison to that observed in the direct method, the suitable curve must be chosen by considering a way of measurment.

Since the principle of high frequency titrations is considered to be a factor in total impedance, it is difficult to clarify the principle only by these curves.

Eig. 11a.
Theoretical Curve of Parallel (indirect)



Fia. 11b.
Experimental Curve of Series (indirect)



II. Concentration Curve

In order to explain the concentration curve of high frequency titration, the receiver-type circuit (Fig. 2) was used. The equivalent circuit of this can be set as a result of preliminary experiment, as is shown in Fig. 12, E=high frequency electromotive force in the receiver coil, L=inductance of the coil, R_L=ohm resistance of the coil, V=voltage between both edges of the coil.

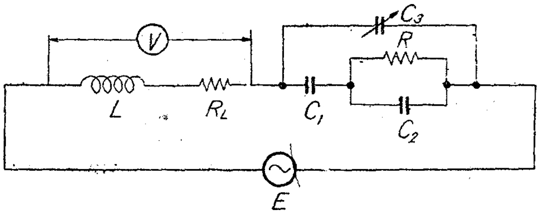


Fig. 12

Under the voltage which serves as an indicator of titration, if the electric current caused by the change in a concentration is termed I, voltage, V, should be $Z = (jWL+R_L)I$

$$V = \frac{E}{Z_0}(jWL+R_L), \qquad Z_0 = \text{Total impedance}$$

$$Z_0 = R_L+j\omega L+\cfrac{1}{j\omega C_3+\cfrac{1}{\cfrac{1}{j\omega C_1}+\cfrac{1}{\cfrac{1}{R}+j\omega C_2}}}$$

In the case of non-adjusting condenser, C_3, the calculation is simple. The C_1, C_2, and R_2 in the equivalent circuit of the electrodes are transferred into the series form of preliminary expriment (8) and (9), then series impedance can be calculated taking the factor of coil, L. In general, usual titrimeters have an adjusting condenser, C_3, the calculation should be made as follows:

The electrode circuit should be converted into parallel according to Equations (10) and (12), then after adding (or taking) C_3, it is converted into series form. After adding L on the vector, the total impedance should be calculated. The calculation is made on the principle mentioned above. The calculation is made on the following values which are close to the actual case:

Area of the electrode, $F \doteqdot 1.5\,\text{cm}^2$, thickness of the beaker, 1 mm. (actually, both sides of the beaker are counted and this should be 2 mm.).

DK of glass, $\varepsilon \doteqdot 8$

Distance between electrodes, $d = 2$ cm.

The solution is, $C_1 \doteqdot 5$ p.f., $C_2 \doteqdot 10$ p.f.

(the assumption is, $f = 10^6\infty$, $L = 1.10^{-3}$H, $C = 20$ p.f.), in the vicinity of balance when C_3 is used.

Taking R as a variable, the change in V on the meter of the titrimeter is obtained as a, b, c, and d in Fig. 13, which fully explain the concentration curve shown in Fig. 1. This resembles the concentration curve by coil electrode.[11~14] The curve by the condenser electrode is caused by the condenser of tuned coil and it is shown that the location of the peak is quite different from that

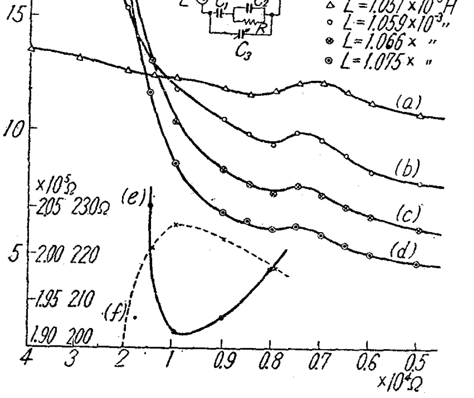


Fig. 13.

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11) M. Honda, Y. Yoshino, T. Abiko: J. Chem. Soc. Japan, **74**, 371 (1953).
12) K. Nakano: *Ibid.*, **74**, 142 (1953).
13) S. Fujiwara, S. Hayashi: *Ibid.*, **74**, 171 (1953).
14) Y. Kamura: J. Pharm. Soc. Japan, **74**, 1 (1954).

obtained by the following equations which have been used so far:

$$R = \frac{1}{C\omega}\ \text{(series)}\ ,\qquad R = \frac{1}{\omega(C_1+C_2)}\ \text{(parallel)}.$$

1) Peak on the concentration curve $R \fallingdotseq 0.8\times10^4\Omega$ (Fig. 13, b, c, d)
2) Peak of loss in parallel form of electrode $R \fallingdotseq 1.0\times10^4\Omega$ (Fig. 13, e)
3) Whole circuit is converted into series form $R \fallingdotseq 1.0\times10^4\Omega$ (Fig. 13, f)

The shape of curve is dependent on the C_3 and C_1/C_2.
The example for this will be reported at a later date.

Conclusion

In order to interpret the concentration curve of high-frequency titrimeters, it is not necessarily correct to calculate C and R of a series or parallel form of an equivalent circuit without any suitable measurement. In many cases of high frequency titrimeter the mechanism from which the concentration curves are drawn out is too complicated to be interpreted by the calculation of C and R of series or parallel form.

By employing the receiving type titrimeter, however, the calculations of the concentration curves have now been realized.

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Summary

Studies on the theory of high-frequency analysis are becoming numerous but some of their reports contain doubtful points as to the formulation of such theories. The present studies were made in order to examine the method of theoretical formulation and it has become clear that different experimental results are obtained from identical phenomena according to the method of measurements employed.

In formulating a theory in high-frequency analysis, the point to note is the actual method of measurements. In other words, a theoretical formulae which agree with the method of measurements must be obtained. The variations of electric current, electric voltage, and cycles measured by oscillating or receiver type cannot be directly explained by the results obtained through measurement by the bridge.

In order to explain theoretically the experimental results obtained by the analytical apparatus currently used, high frequency wave was directly applied to solutions and the nature of the changes were examined by the bridge. Correlation of such a change and indirect measurement through the wall of the beaker was sought. Based on there results, a theoretical formula which would support the method of measurements by the currently used analytical apparatus was obtained. By making concrete calculations, uniform explanations for concentration curves in general were made. Some improvements were also made for drawing up theoretical curves for the existing indirect measurement.

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