U.D.C. 545.37.082.7

61. **Yoshihiro Maekawa**: Studies on the Higher Derivative Automatic Titration. II[1]. Theoretical Considerations. (2).

(*Osaka College of Pharmacy,* and The Institute for Chemical Research, University of Kyoto*)

In the preceding paper,[1] it was shown that in ordinary potentiometric titrations, it is the best to use the 3rd derivative voltage as the triggering signal for the automatic titration. In this paper is presented the theory of the automatic titration in which the input voltage changes as shown in Fig. II-1 or -2, during titration.

(A) Automation of the titration with titration curve as in Fig. II-1.

The titration curve is shown in bimetallic electrode titration, constant current polarising titration, etc., and the end point matches the maximum point, and the titration curve is analogous to the 1st derivative voltage curve (Fig. I-5) of the ordinary potentiometric titration (Fig. I-4).

In this paper, therefore, let $e_1(t)$ be the input voltage which represents the titration curve as in Fig. II-1, and with $\mathfrak{L}$-transform $E_1(p)$.

$$E_1(p) = (1 - \mathcal{E}^{-hp})^2/h^2p(p + 1/\tau) \quad \text{(II-1)}$$

(cf equation (I-3))

τ in the above equation is not always equal to the τ of the differentiation circuits of the automatic titrator, but it will be assumed that these two τ's are the same. Even if two τ's are not the same, it is easy to calculate the response.

Under these assumptions, it may be easily seen that nth derivative voltage of $e_1(t)$ by R-C differentiation networks is identical to the $(n-1)$th derivative voltage of $e_0(t)$.

So, in the automation of this titration, the following will be expected:

1) 2nd differentiation is the best.
2) 1st differentiation is usable.
3) 3rd differentiation is not usable.

In these treatments, however, it will be noted that the theoretical end point of the titration is the maximum point in Fig. I-5, and does not match the point $T=1$.

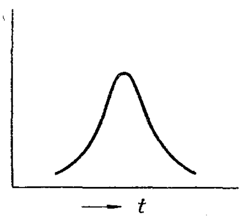

Fig. II-1.

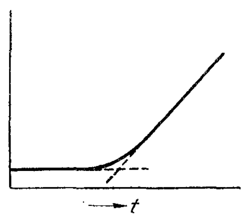

Fig. II-2.

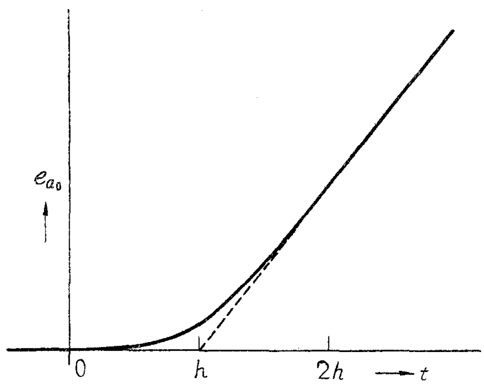

Fig. II-3. Input Voltage Curve (e_{a0})

(B) Automation of the titration which has the titration curve as in Fig. II-2.

It can be easily seen that the 1st derivative voltage curve of this titration curve

* Kitayashita-mura, Minamikawachi-gun, Osaka-fu (前川義裕).

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will be the curve analogous to $e_0(t)$[1](Fig. I-4). So, in this section, let $e_{a0}(t)$ be the input voltage representing the curve as in Fig. II-2, with $\mathfrak{L}$-transform $E_{a0}(p)$ which is the integral of $E_0(p)$.

$$E_{a0}(p) = (1 - \varepsilon^{-hp})^2/h^3p^3 \qquad \text{(II-2)}$$

Thus, $e_{a0}(t)$, that equals $\mathfrak{L}^{-1}[E_{a0}(p)]$, is given by

$$e_{a0}(t) = \frac{1}{2\pi j}\int_{c-j\infty}^{c+j\infty} \frac{(1-\varepsilon^{-hp})^2\varepsilon^{pt}}{h^3p^4}\,dp \qquad \text{(II-3)}$$

Let

$$f_{a0}(t) = \frac{1}{2\pi j}\int_{c-j\infty}^{c+j\infty} \frac{\varepsilon^{pt}}{h^3p^4}\,dp \qquad \text{(II-4)}$$

Then

$$e_{a0}(t) = f_{a0}(t)\cdot H(t) - 2f_{a0}(t-h)\cdot H(t-h) + f_{a0}(t-2h)\,H(t-2h) \qquad \text{(II-5)}$$

$$f_{a0}(t) = t^3/6h^3 \qquad \text{(II-6)}$$

Equation (II-5) and (II-6) give the input voltage $e_{a0}(t)$, and are plotted in Fig. II-3, which is the same as the anticipated curve.

Now, let $e_{an}(t)$ be the nth derivative voltage of $e_{a0}(t)$ by R-C differentiation circuit, with $\mathfrak{L}$-transform $E_{an}(p)$. Then, from equation (I-3),

$$E_{an}(p) = p^nE_{a0}(p)/(p+1/\tau)^n \qquad \text{(II-7)}$$

$$(n = 1, 2, \ldots\ldots\ldots\ldots n.)$$

$$E_{a0}(p) = (1-\varepsilon^{-hp})^2/h^3p^{3-n}(p+1/\tau)^n \qquad \text{(II-8)}$$

Thus, $e_{an}(t)$, the response function that equals $\mathfrak{L}^{-1}[E_{an}(p)]$, is given by

$$e_{an}(t) = \frac{1}{2\pi j}\int_{c-j\infty}^{c+j\infty} \frac{(1-\varepsilon^{-hp})^2\varepsilon^{pt}}{h^3p^{4-n}(p+1/\tau)^n}\,dp \qquad \text{(II-9)}$$

Let

$$f_{an}(t) = \frac{1}{2\pi j}\int_{c-j\infty}^{c+j\infty} \frac{\varepsilon^{pt}}{h^3p^{4-n}(p+1/\tau)}\,dp \qquad \text{(II-10)}$$

then,

$$e_{an}(t) = f_{an}(t)\cdot H(t) - 2f_{an}(t-h)\cdot H(t-h) + f_{an}(t2h)\cdot H(t\,2h) \qquad \text{(II-11)}$$

Calculated results of $f_{an}(t)$ for $n = 3$ and $n = 4$ are as follows:

$$f_{a3}(t) = \tau^3\{2 - \varepsilon^{-t/\tau}(2 + 2t/\tau + t^2/\tau^2)\}/2h^3 \qquad \text{(II-12)}$$

$$f_{a4}(t) = t^3\varepsilon^{-t/\tau}/h^3 \qquad \text{(II-13)}$$

Simplifying by putting $T = t/h$, $\alpha = \tau/h$, one gets

$$e_{an}(T) = f_{an}(T)\cdot H(T) - 2f_{an}(T-1)\cdot H(T-1) + f_{an}(T-2)\cdot H(T-2) \qquad \text{(II-14)}$$

$$f_{a3}(T) = \alpha^3\{2 - \varepsilon^{-T/\alpha}(2 + 2T/\alpha + T^2/\alpha^2)\}/2 \qquad \text{(II-15)}$$

$$f_{a4}(T) = T^3\varepsilon^{-T/\alpha}/\alpha^3 \qquad \text{(II-16)}$$

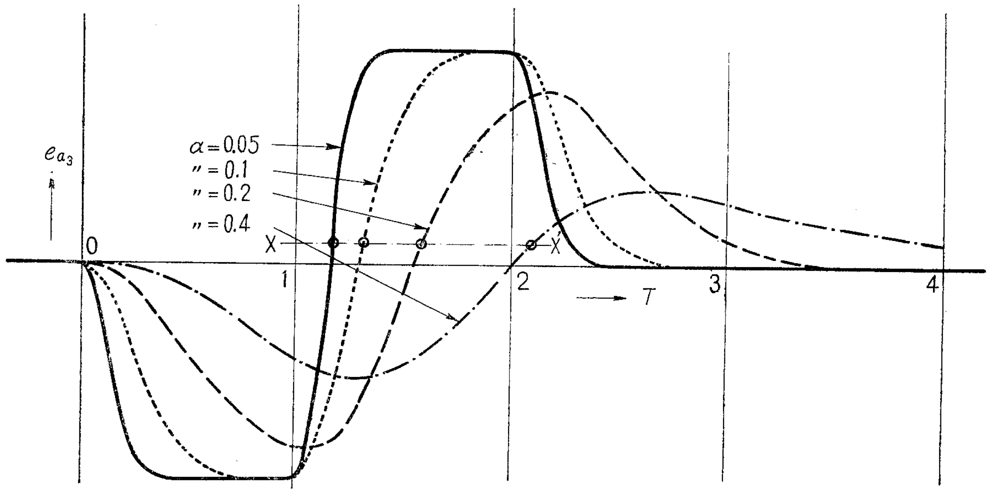

Fig. II-4. 3rd Derivative Voltage Curve of e_a (e_{a3})

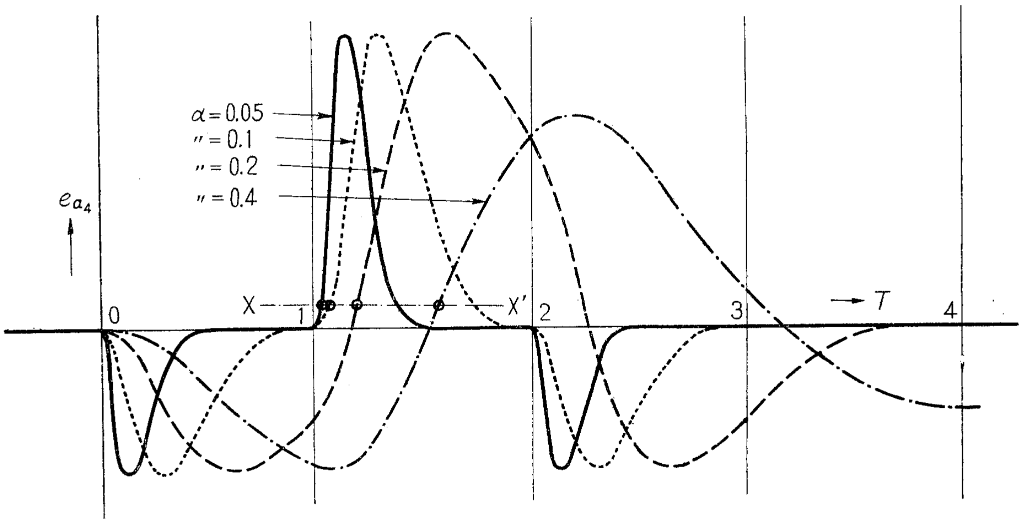

Fig. II-5. 4th Derivative Voltage Curve of e_a (e_{a4})

Equations (II-14) and (II-15), and (II-14) and (II-16), give the responses of the 3rd and 4th differentiation circuits which are plotted in Figs. II-4 and II-5, respectively.

From the comparison of Figs. II-4 and II-5, it will be expected that the 3rd differentiation may be used but 4th differentiation may be more properly used for this automatic titration.

The calculations are not presented here, but from the preceding paper and above considerations, it will be easily seen that 1st, 2nd, and 5th differentiations may not be used.

In the above discussion, how many order differentiation voltage, as the triggering signal, should have been used for practicing the automatic titration with the least titration errors, was considered only from the response of the differentiation circuits. The following points should, however, be noted :

1) The *R-C* differentiation circuit will lose output voltage, so that more amplification is needed for larger order of differentiation, and there will be inevitably found the difficulty of making automatic titrator. A more insertion of vacuum tube amplifiers give rise to the more amplifying gain and become sensitive to inducement of alternative current (" hum "). To avoid the humming, a high-pass filter was inserted at the top of the automatic titrator (this filter also acts to decrease the small change of input voltage by stirring the titration liquid, etc., during the titration), and a negative feedback used which is effective in a high frequency range (the input voltage is below few cycles, so the high frequency indicates above ca. 10 cycles).

2) In general the titration, with a titration curve as in Fig. II-2 and the end point of which is obtained as the intersection of two straight lines, is useful in case the measured values near the end point have little significance (e.g. in case solubility of the product is not so great in the precipitation titration).

3) The inflection point of the 1st derivative curve of these titration curves does not always match the end point (intersection of two straight lines in the titration curve).

Namely, these titrations may be stopped automatically near the end point by using the 3rd or 4th derivative voltage as the triggering signal, but it has little significance, and the titration error will be greater than that of the automatic titration of normal potentiometric titration or the titration described in section (A).

If the electrodes are chosen properly, many titrations may be automatically stopped by using 2nd or 3rd differentiation, and the above automatic titration is not necessary.

In the above titration we get the output, generally, as current, conductivity, etc., so we must change these output to voltage proportional to these output before the differentiation, and these changes have many difficulties. So, the automation of the above titration by higher differentiation is not considered a good method.

The author thanks Prof. Seishi Takagi of the University of Kyoto and Dr. Saburo Kakinuma, President of the Osaka College of Pharmacy, for their interest and encouragement in this work, and Assist. Prof. Bunji Kondo, Electrical Engineering Dept., Engineering Faculty, University of Kyoto, for kind suggestions in this work.

Summary

In the titration with a titration curve as in Fig. II-1, it is the best to use the 2nd derivative voltage as the triggering signal and the 1st derivative voltage may be used, too.

In the titration with a titration curve as in Fig. II-2, the 3rd or the 4th derivative voltages could be used for the automatic titration, but by the above reasons, it is not a good method.

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62. **Yoshihiro Maekawa**: Studies on the Higher Derivative Automatic Titration. III.[1] The 3rd Derivative Automatic Titrator, AT-V, and Results of Titration with AT-V.

(*Osaka College of Pharmacy,* and The Institute for Chemical Research, University of Kyoto*)

In the preceding paper,[2] it was shown that in the normal potentiometric titration, it is the best to use the 3rd derivative voltage as the triggering signal.

This paper deals with the 3rd derivertive automatic titrator, AT-V, and the results obtained with it.

Figs. III-1, III-2, and III-3 respectively show the electrical wiring diagram of AT-V, the exterior view of AT-V, and mechanism of the magnetic cock used in AT-V.

The principle of AT-V is the same as that of the 2nd derivative automatic titrator, AT-III.[3] The electromotive force, which is obtained from the titration vessel, is added to the high-pass filter which is constructed with two resistors, 250 kΩ each, and a condenser, 2 μF. Then it is amplified and differentiated with *R-C* differentiation network. The amplification and the differentiation are repeated three times, thus the 3rd derivative voltage, is obtained. For the amplifiers, differential amplifiers are used to decrease the hum and increase the gain in low frequency range. The negative feedback, which is constructed with two 250 pF condensers, C_2's, and effective in high frequency range, are also used to decrease the hum. The 3rd derivative output voltage is amplified, then put on the cathode follower circuits for decreasing the direct current level and impedance. The output voltage, adjustable by VR_2 and VR_3, are used for the triggering voltage of the thyratrons. The thyratrons, 66G-GT's, are operated by alternating current, though in the 2nd derivative automatic titrators, AT-I, -II,

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* Kitayashitamura, Minamikawachi-gun, Osaka-fu (前川義裕).

1) Part II : This Bulletin, 4, 325(1956). 2) Part I : This Bulletin, 4, 321(1956).
3) Y. Maekawa : Japan Analyst, 3, 489(1954).