Signal Conversion for the Automation of Titrations

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Summary. By following a special system of signal conversion an universally applicable automatic titrator can be developed. Independently of the used titration technique the signals are converted into a signal that as a function of the added volume has got the shape of a step function. This step signal of which the jump within the titration error coincides with the equivalence point is finally used to drive the apparatus and to let it stop in the jump.

Introduction

For the automation of titrations two different ways can be followed. One way is to registrate the titration signal as a function of the added volume with a printer, on a tape, in a computer memory or more simply with a recorder, and to determine the equivalence point afterwards from the registration. This system can be applied to nearly every titration technique.

Following the other way in which the titration apparatus stops in the equivalence point, problems arise when we want to develop one universally applicable titrator because of the diversity in techniques and methods for the determination of the end-point.

In this paper it will be shown that by applying a special system of signal conversion a relatively simple titrator can be developed suitable for all end-point techniques such as potentiometry (pH, pH, oximetry), photometry, conductometry, amperometry (dead stop) and voltametry. Use is made of the fact that nearly all titration signals can be converted in electric potentials, which, just like the logarithmic signals from potentiometric titrations, show a jump near the equivalence point on adding the titrant.

The main operation performed to the titration signals is a differentiation to the volume. This can electronically be done in a simple way if the titrant is added to the reaction system in small, exactly equivalent portions. The stepwise liquid addition can be realized with a piston- or plunger-buret coupled to a step-motor, which is driven by electric pulses. With this driving system the motor turns a constant small angle after every added pulse. The pulse driving system can be a pulse generator that has a constant frequency or preferably a frequency which is proportional to a voltage difference \( \Delta V = V_t - V_e \) in which \( V_t \) is the converted titration signal and \( V_e \) a constant voltage that determines the end of the titration and that is selected before starting the titration. \( \Delta V \) will change sign during the titration if \( V_e \) is suitably selected. This should occur with a jump. When the end point is approached, the pulsfrequency will decrease. The frequency becomes zero when the endpoint is reached or slightly passed. So the titrator stops automatically near the end-point. The systematic error depends on the place and the steepness of the jump and on the selection of \( V_e \).

It can be noted that the steeper the jump, the less critical \( V_e \) has to be selected.

The outlined measurement and control system (with exception of the differentiation to the volumes) has already been applied in the commercially available automatic titrator of Mettler Instrumente, A.G., Switzerland. This titrator has been developed for all kinds of potentiometric titrations.

In the following it will be shown, that other signals than electrode potentials after conversion can be combined with the same control system, and that this leads to a very suitable universally applicable automatic titration system.
For that purpose first the agreement between the converted signals of different techniques will be considered and finally the way in which conversion practically can be realized.

Form of the Converted Signals
The agreement between the titration signals of the different techniques after conversion is actually caused by the break which all signal-volume curves show near the equivalence point. For a number of techniques it will be shown that this break after differentiation leads to a signal-volume curve with a jump near the equivalence point. In the case of photometric titrations the transmission $T$ is measured vs. the volume. If, for instance, a metal in low concentration ($C_M = 10^{-4}$ M) is titrated with EDTA in the presence of indicator added in excess, a curve is obtained as in Fig. 1. The relation between the titration parameter $t$ (proportional to the volume) and the relative concentration $m_i = [M]/C_M$ (proportional to log $T$) is given by [1].

$$f = 1 - m_i - \frac{1}{Z_t} \cdot \frac{1}{1-m_i/\beta} + \frac{1}{m_i} \cdot \frac{Z_t}{Z_M}$$

For an accurate titration the following titration conditions have to be satisfied: $Z_t > 10$ and $Z_M/Z_I > 3000$ [1]. Bearing this in mind we can calculate $(dmi/dt)$ for the points: $f = 0.95$, $f = 1.00$ and $f = 1.05$. The approximate values are respectively $-1$, $-1/2$ and 0. As additionally $(dT/dt) \sim T \cdot (dmi/dt)$ and as $T$ may be considered as constant near the equivalence point, it follows that in the equivalence point the tangent to the curve has a value which can be approximated by the mean of the values before and after the equivalence point (Fig. 1). It can reversely be said that the equivalence point corresponds to the middle of the jump in the differentiated transmission signal vs. $t$. If now $V_e$ is selected halfway the jump the titration will stop automatically in the equivalence point.

From Fig. 1 it follows that the titration will have starting difficulties, as $V_t < V_e$ for $f = 0$. This problem can be solved by following a special starting procedure. As this is only a practical problem it will be discussed in the next section.

In the amperometry use is made of polarized electrodes. Two cases can be distinguished. In one case the electrode couple contains a polarized electrode vs. a standard electrode, in the other case both electrodes are polarized. In both cases a small potential is forced to the cell and the current is measured. The voltametry only differs from this by that the current is forced and the voltage is measured. In all four cases signal-volume curves are obtained which have a rather sharp break near the equivalence point. In Fig. 2 two examples are given. In Fig. 3 the respective curves differentiated with respect to the volume are given. Again jumps occur near the equivalence point.

![Fig. 1. The transmission curve $T$ is experimentally found in the titration of Cu (1 µM in a 10 ml cell) with EDTA in the presence of TAR (1,2 µMol) as indicator. The curve $(dT/dt)$ is equivalent to the respective curve obtained by differentiating $T$ to the volume. $A$ indicates the point in which the apparatus is switched from constant pulse rate to automatic end-point approach in order to overcome start difficulties. $A > 0$ is advisable in order to prevent a too slow rate just after $A$.](image1)

![Fig. 2. The curves $a$ and $b$ represent the forms which are obtained in Karl Fischer titrations and Fe-Ce titrations.](image2)