Derivative Thermometric Titrations Employing Operational Amplifier Instrumentation

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ABSTRACT

An improved derivative thermometric titration apparatus designed around operational amplifiers is described which is capable of monitoring the small temperature change and of computing the derivatives for accentuation of the titration end point that is difficult to locate by extrapolation methods. The instrument is constructed of four commercial operational amplifiers. A use of dummy cell provides the subtraction means for compensation of the initial temperature and random temperature fluctuations with a resultant gain in signal-to-noise ratio. The successive differentiation action of the computer has been nearly "perfect," so that the two breaks (blank or starting and end point) of the titration curve can be located with the precision of 0.2% by observing two peak points on the second derivative curve. Arrangements useful in obtaining such a good derivative response that is exactly proportional to the input signal are discussed. Plots of the enthalphogram and its derivatives are presented, with the results of several titrations used to evaluate the performance of the apparatus.

INTRODUCTION

Many recent uses and advantages of operational amplifiers (OA) in analytical instruments have been described. They involve chiefly the applications of OA to control and measurements, wave form generation, etc. From the point of view of analog computers, however, the differentiation action of the computer, useful in many types of derivative plotting and for the automation of titration, has received little attention. A few examples are the derivative polarograms and gas chromatograms.
in which the slopes of the curve to be differentiated are large and nearly free from noises of high frequency type.

The thermometric titration, widely recognized for its utility in analytical and fundamental applications, has inherent difficulty in end point locating by the fact that the end point region may be "rounded" or the difference in slopes of the linear portions of the curve, on either side of the end point, may be rather small. Zenchelsky and Segarto discuss the titrations in derivative modes for the accentuation of the end point region, thus the gaining in the precision of selection of the end point may be resulted. In thermometric titrations, however, the low output voltage of the thermistor bridge,

![Block diagram of apparatus](image)

**Fig. 1. Block diagram of apparatus**

The numbers in each of the functional blocks denote the number of operational amplifiers of Heath Model EUW-19A OA system. The Recorder 1 was 100mV., 1 or 10mV. full-scale for 2 and 3.

the slow attainment of thermal equilibrium within the titration vessel and the random fluctuation in temperature resulting a small signal-to-noise ratio pose rather involved problems for the successive differentiations.

The present introduction of titration apparatus based on OA for the measurement and acquisition of derivatives offers a number of advantages over the conventional procedures, as a natural extension of the capability of replacing much of the specific chemical-instrument circuitry by analog computing circuitry.

**EXPERIMENTAL**

**Transducer and Measuring Circuit.** Two matched thermistors \( R_a \) and \( R_s \) in Fig. 2A constitute ratio arms of the temperature sensing bridge (Fig. 1), the other two arms are the variable voltage sources, \( E_a \) and \( E_b \). This configuration makes the transducing of temperature easy and sensitive than conventional bridge arrangement, looking from the measuring amplifier, OA #1. Thus the governing relation

\[
\frac{V_a}{V_s} = \frac{R_s - R_3}{R_1 - R_4} \quad \text{[V:13V., mercury battery]}
\]
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\[ e'_2 = -R_s(E_s/R_a - E_0/R_0) \] \hspace{1cm} (1)

where \( e'_2 \) denotes the output voltage as a whole and the drift and offset of the amplifier are neglected by use of the stabilized amplifier \( P \) (implied by the small, overlapping triangle in Fig. 2A) and sufficiently large gain is supposed. If initial temperature is compensated by \( R_s \) used with \( R_t \) and \( E_p \) the recorded output voltage, for the temperature change \( \Delta T \) as the titration proceeds, may be denoted simply as

\[ e_2 = R_s E_s \xi \Delta T/R_0 \] \hspace{1cm} (2)

after substitution the expression for negative temperature coefficient of the thermistor to the derivative of the equation (1) with respect to \( R_s \), and \( \alpha \) is the temperature coefficient at \( R_0 \), the initial or balanced resistance of the thermistor \( R_s \).\(^{17}\) With \( \alpha = -0.04 \), \( E_s = 1.0V \), \( R_s/R_0 = 50 \), and \( \Delta T = 0.03 \degree C \), the typical values encountered in thermometric titration, \( e_2 \) yields about 60 mV, so that it can be subjected directly to differentiation without further amplification. This output was suitable for 100 mV fullscale recorder through attenuator and damping circuit which has a time constant of two seconds.

The measuring thermistor \( R_s \) is the input resistance of the computer as in conductance meter\(^{18}\) and photometric circuits.\(^ {19} \) The subtracting action of the initial temperature compensating circuit provides the zero adjuster for normal titration and bucking voltage source for differential titration.\(^ {19} \) An alternative compensation method in which the operation of the measuring amplifier as a differential amplifier by applying the positive \( E_s \) to non-inverting input has been avoided in practice, because of the unstability of the circuit.

**Successive Differentiation.** The output voltage of the measuring amplifier, the regular titration curve, is fed directly to the differentiating network using an amplifier, which is shown in Fig. 2B. As pointed out elsewhere,\(^ {19} \),\(^ {20} \) the shunt capacitor associated with feedback resistor, which has the corner frequency of the order of hundreds cycles, was necessary for obtaining a good derivative response. Because of the double differentiation with T-networks using an amplifier was unsuccessful, successive differentiation was desired for the second derivatives. With the particular amplifier used, it was inevitable to insert an amplifier with preceded low-pass filter between the consecutive differentiating circuits for a discernible response, \( e_2 \) from noise.

A modification in the arrangement, such that the consecutive differentiator is followed by the voltage amplifier, was used for the cases where only the location of the end point is the primary interest. This change has increased the over-all signal-to-noise ratio at the sacrifice of signal fidelity.

**RESULTS**

With the thermometric cell constant of 0.0096 Kcal./\degree C, titrant delivery rate of 0.808 ml
/min., the operational results of a typical titration are depicted in Fig. 3. Through whole the titrations, the dummy thermistor $R_0$ was immersed into the Dewar flask containing the titrant and being stirred at the same rate with the titration cell. This use of dummy cell, instead of common resistor as in the conventional thermistor bridge, allows the damping circuit of smaller time constant is useful, thus introducing a smaller response lag to the resultant derivatives. (Fig. 3).

In the second derivative curves, the end point nearly coincides with the maximum peak point, and is affected by the time constant of the filter employed, as is expected. Because of the blank peak which would lag or shift in same degree, however, this does not mean a uselessness of the method. This procedure requires a minimum of the point-choosing considerations, for the distance between the two peaks may be given precisely and accurately.

The resultant data obtained from several titrations by this procedure are shown in Table 1.

In connection with the sensitivity, the derivative technique does not increase the lower limits in concentration of the titrate, with the particular computer system employed. This can be expected from that the transduced signal level and the required amplification are determined principally by the concentration of the solution to be titrated. For the regular and differential mode, the measuring unit using an amplifier (Fig. 2A) is ideally suited for the titration of very dilute solution (10^{-4} M or less) with a reasonable accuracy.

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