Apparatus for Automatic End Point Determination in Thermometric Titrations

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An apparatus suitable for automatic end point determination in thermometric titrations is described and evaluated. The apparatus is capable of detecting end points for a fairly wide variety of titration curve (enthalpogram) shapes and appears to be satisfactory for routine analyses, such as those involved in control procedures.

PRIESTLEY (1) has described an instrument for the automatic determination of end points in routine thermometric titrations. This paper reports the details of an apparatus for the same purpose constructed using, for the most part, equipment already in service in our laboratory. It is becoming increasingly apparent that thermometric titration has wide analytical applicability. In a recent communication (2), some possible applications of thermometric titration to pharmaceutical analysis were pointed out. Additional work along these lines is now in progress.

In a thermometric titration, the end point is manifested as a change in slope in a plot of temperature versus volume of titrant added (enthalpogram[1]). For a case in which the reaction is incomplete at the stoichiometric point, the end point is obtained by extrapolation of the two straight-line portions of the plot. In the first derivative of such a curve, the end point appears as an inflection point. A first-derivative thermometric titration curve, therefore, resembles an original potentiometric titration curve (potentiogram). Similarly, a third-derivative enthalpogram resembles a second-derivative potentiogram, in that the end point corresponds to the point where the curve crosses the abscissa after an initial rise. The instrument described by Priestley (1) utilizes the first derivative of the potential across a thermistor

to locate the end point, whereas the apparatus described in this report uses the third derivative of the imbalance potential of a Wheatstone bridge, one arm of which is a thermistor. Derivative thermometric titrations have been described by Zenchelsky and Segatto (4).

DESCRIPTION OF APPARATUS

The imbalance potential of a thermistor bridge circuit, similar to that described by Jordan and Alleman (5), is amplified, filtered, differentiated, and fed into the control unit of a Sargent-Malmstadt automatic (potentiometric) titrator. The latter is designed to amplify and differentiate a signal twice and, *via* a two-thyratron switching circuit, to trigger a relay system which controls a 115-v. a.c. supply to a buret. The thyratron switching circuit, activated by the rise of the positive half of the second-derivative (of the input to the control unit) potential, fires when the second-derivative potential crosses the zero line. A block diagram of the entire apparatus is shown in Fig. 1.

To amplify the imbalance potential of the thermistor bridge, we used the servo mechanism from a 5-mv. Bristol Dynamaster recorder. A 1700-ohm "retransmitting slidewire," available from the manufacturer, was attached, and provision was made for applying a potential of 0–45 v. d.c. across the resistance. The slide contact of the retransmitting slidewire is coupled to the slide of the balancing potentiometer. Thus, gains of up to 9000 are achieved. Other methods of amplification were not investigated.
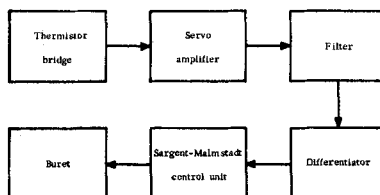
[1] The authors and other workers in this field have previously used the term "thermogram" to describe such plots. Since thermogram is usually used to denote differential thermal analysis plots, we have adopted the terminology suggested by Pendergrast (3).

Fig. 1.—Block diagram of automatic thermometric end point determination apparatus.

Figure 2 shows the circuit diagram for the only "new" equipment in the apparatus. Not shown are the thermistor bridge, the servo balancing unit, and the Sargent-Malmstadt control unit. The components represented by Fig. 2, except for the previously described retransmitting slidewire, P3, are all contained in a $9 \times 5 \times 6$ in. metal cabinet. The relays are shielded by an aluminum box, indicated in the lower portion of the diagram, in order to prevent field effects.

The time constant of the R.C. filtering circuit, C2-P2, was varied by adjustment of P2. For most titrations, P2 was set at $\sim$25,000 ohms to provide a time constant of $\sim$2.5 sec. At such a setting, variations in the resistance, due to the positions of the P1 and P3 slides, have little effect on the time constant of the filter. The filter circuit is necessary to prevent signal noise, due to instantaneous thermal inhomogeneities in the titration cell, from causing spurious firing of the control unit circuit. The differentiator circuit, C1-R1, has a time constant of 0.5 sec. The filter and differentiator circuits are similar to those of Zenchelsky and Segatto (4).

The filtered differentiated signal is introduced, *via* plug PL1, into the phono jack on the Sargent-Malmstadt control unit. The control unit was originally equipped with a 10-sec. thermal delay relay which prevents false firing due to a voltage surge at the beginning of a titration. It was necessary to replace this relay with one having a 15-sec. delay.

The control unit supplies 115 v. a.c. to a three-prong microphone jack during a titration and shuts off the power at the end point. This 115-v. a.c. supply is introduced into plug PL2 and used to control one of two burets: (*a*) a 5-ml., gravity-flow glass buret (hereafter referred to as manual buret) or (*b*) a 3.2-ml., 0.6 ml./min., constant flow Aminco Menisco-matic buret (hereafter referred to as automatic buret). The tip of the manual buret was connected to a piece of neoprene tubing, which passed through a solenoid valve supplied with the Sargent-Malmstadt titrator. The solenoid, which was plugged into the receptacle, SK2 (labeled normal), permitted the titrant to flow until the end point was reached, and the 115-v. a.c. supply terminated. The rate of flow of the manual buret was adjusted with a clamp on the neoprene tube. The automatic buret, which has a synchronous motor and a digital counter calibrated in volume of titrant dispensed, was plugged into the receptacle, SK1 (labeled brake). During the titration, relay K2 kept SK1 attached to the 115-v. a.c. source from the control unit. At the end point, when the a.c. supply was terminated, relay K2 switched SK1 to a d.c. source. (See Fig. 2.) The d.c. signal served to brake the synchronous motor of the buret and thus efficiently prevented coasting after the end point was reached.

TITRATION PROCEDURE

One hundred milliliters of solution was placed in a small cylindrical Dewar flask. The flask was stoppered with a neoprene stopper through which was inserted a 2000-ohm bead-in-glass-probe thermistor, a right-angled titrant delivery tip, and a glass stirrer with four quadrantal blades. The stirrer passed through a Teflon bearing in the stopper. The thermistor extended to $\sim$3 mm. above the blades of the stirrer. It was found that the mini-

mum signal noise occurred when (*a*) the stirring rate was adjusted to just below the point of sputtering of the solution, and (*b*) the delivery tip was positioned so that the flow of titrant was counter to the flow of the solution and so that fluid in the vicinity of the tip had to make almost a complete loop in the flask before reaching the thermistor.

When the automatic buret was employed, the play in the gear mechanism was taken up by hand prior to the start of a titration.

No advantage was gained by waiting until thermal equilibrium in the titration vessel was attained before starting the titration. The titration was initiated a few seconds after the stirrer was turned on by depressing the "automatic" push-button switch on the control unit. The buret shut off automatically when the end point was reached. The titration volume was read either from the graduation marks on the manual buret or from the digital counter on the automatic buret.

The control unit of the Sargent-Malmstadt titrator contains a "bias adjustment" which determines the minimum *amplitude* of the third-derivative (second derivative in a potentiometric titration) peak voltage necessary to actuate the relay system. This adjustment was used to eliminate spurious firing due to line and circuit noise. The third-derivative peaks due to *signal* noise, which was not eliminated by the filter (C2-P2 in Fig. 2), were, except for cases of very sharp end points, of about the same magnitudes as the peak voltages due to the end points. Thus, the bias adjustment generally could not be used to eliminate spurious firing due to signal noise and was seldom readjusted.

The two factors which had to be adjusted to suit individual titration systems were the voltage across the retransmitting slidewire (adjusted with S1 and P1 in Fig. 2) and the setting of the "discriminator adjustment" on the control unit. The latter adjustment serves to determine the minimum *duration* of
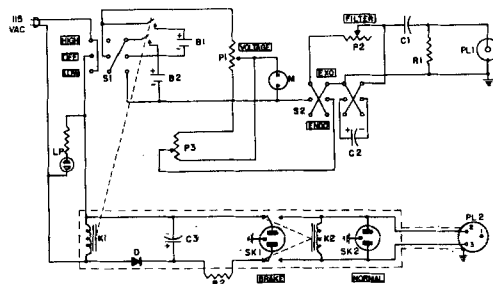
Fig. 2.—Filtered differentiator and auxiliary circuits. Key: B1,B2, 22.5-v. batteries; C1, 0.5-microfarad, 400 w.v. d.c. paper-insulated capacitor; C2, 100-microfarad, 50 w.v. d.c. electrolytic capacitor; C3, 20-microfarad, 250 w.v. d.c. electrolytic capacitor; D, 1N1491 silicon rectifier; K1, 115-v. a.c., DPST relay; K2, 115-v. a.c., DPDT relay; LP, neon indicator lamp; M, 0–50 v. d.c. voltmeter; P1, 1000-ohm, 1-turn, wirewound potentiometer; P2, 50,000-ohm, 1-turn, wirewound potentiometer; P3, 1700-ohm retransmitting slidewire (in amplifier); PL1, phono plug (to control unit); PL2, 3-prong microphone plug (to control unit); R1, 1-megohm, 1-w. resistor; R2, 1500-ohm, 10-w., wirewound resistor; S1, 3PDT toggle switch; S2, 4PDT lever switch; SK1, SK2, U-ground receptacles.
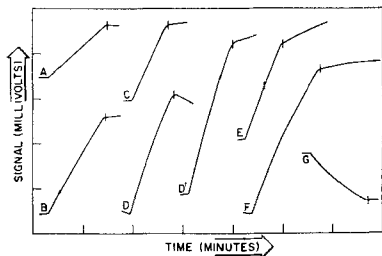
Fig. 3.—Enthalpograms for trial titrations. A, 0.006 *M* HCl *vs.* 1 *M* NaOH, automatic buret; B, 0.01 *M* HCl *vs.* 1 *M* NaOH, manual buret, flow ∼1.1 ml./min.; C, 0.01 *M* H$_3$BO$_3$ *vs.* 3 *M* NaOH, automatic buret; D, D′, 0.02 *M* H$_3$BO$_3$ *vs.* 1 *M* NaOH, manual buret, flow ∼2.7 ml./min.; E, 0.005 *M* H$_3$PO$_4$ *vs.* 3 *M* NaOH, automatic buret; F, 0.01 *M* H$_3$PO$_4$ *vs.* 1 *M* NaOH, manual buret, flow ∼1.8 ml./min.; G, 0.01 *M* MgCl$_2$ *vs.* 1 *M* Na$_4$EDTA, manual buret, flow ∼1.2 ml./min. All concentrations are approximate. The vertical lines indicate the points at which the relay system was actuated. The bridge sensitivity for titration F was 0.85 times the sensitivity for the other titrations.

the positive half of the third-derivative voltage (of sufficiently large magnitude) necessary for activation of the relay system. Fortunately, the third-derivative peaks due to signal noise were of shorter duration than the peaks due to end points. For each titration system, it was necessary to determine a balance between a slidewire voltage sufficient to amplify the end point signal enough to be detected and a setting of the discriminator adjustment sufficient to eliminate firing due to signal noise. A rounded end point required a greater slidewire voltage and more discrimination (longer duration of signal required for firing) than needed for a sharp end point. The proper settings for given systems were found to be reproducible from day to day. In fact, except for cases of very rounded end points, the settings could be varied within fairly broad limits without effect on the performance of the apparatus.

PERFORMANCE

Figure 3 shows recorder tracings of the bridge output signals for some preliminary trial titrations performed to test the ability of the apparatus to detect end points for a variety of titration curve shapes. In these trials, the relay system was used to activate a time pen; the buret was allowed to continue delivering titrant after the end point had been detected. The titration branches of the curves obtained using the manual buret are not linear since the rate of flow decreased as the titrant level decreased during a titration.

End points somewhat less sharp than that exhibited by curve D′ could not be detected without increasing the slidewire voltage to a point where signal noise caused excessive spurious firing. Sharpening of an end point by increasing titrant flow rate permitted the use of a lower slidewire voltage but increased the relative error in the titration volume. (See discussion of lag time below.) With the automatic buret, the apparatus was capable of detecting the first two end points in the neutralization of phosphoric acid. (See curve E.) However, it was pos-

sible to set the voltage and discriminator adjustments so that only the second end point was detected. When the manual buret was used, the curvature in the titration branches made the detection of the first end point unreliable. For such titrations, the adjustments were set to detect only the second end point. (See curve F.)

The apparatus generally performed in a reliable manner. Occasionally, when the slidewire voltage was high, signal noise caused the buret to shut off prior to the end point. Such instances were readily discernible. Unless the spurious firing occurred within 15 sec. (dead time) of the end point, the titration could be resumed without detectable error. During analyses with any particular titration system, a rate of 6–10 titrations per hour was achieved easily when an automatic pipet was employed to deliver solution into the titration flask.

It is apparent from Fig. 3 that there is a lag between the true end point and the response of the relay system. Lag volumes were estimated by comparison with results from classical volumetric titrations and by comparison of automatic titrations of solutions of varying concentrations of the same substance. The results of such estimates are shown in Fig. 4. The datum points in the figure correspond to a wide range of adjustment settings. It appears that the average lag time of ∼0.05 min. was fairly independent of the instrument settings. Priestley observed a similar lag with his apparatus (1), although the lag with the present instrument is much less variable from system to system. In addition, it appears from Priestley's data analysis that for some systems the end point was detected *before* the true stoichiometric point, whereas such behavior was not observed with the present apparatus. It should be noted, however, that Priestley evaluated his apparatus with many more systems than the authors have tried.

Table I shows results of actual analyses. The precision obtained is comparable to that obtained by Priestley. The present apparatus seems to be capable of analyzing solutions of lower concentrations than is Priestley's apparatus.

Included in the table are the results of classical

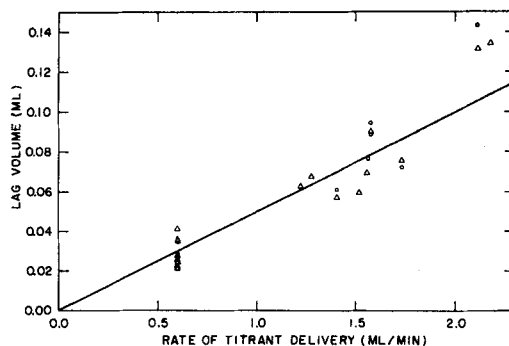
Fig. 4.—Lag in instrument response. Key: Δ, from comparison of automatic and classical (indicator) titrations; ○, from comparison of automatic titrations with identical instrument settings of solutions of varying concentrations of the same substance. (The assumption is made that the lag time is independent of the concentration of the solution.) The solid line represents a lag time of 0.05 min.

TABLE I.—AUTOMATIC THERMOMETRIC END POINT DETERMINATION TITRATIONS

Soln., 100 ml.	Titrant	Titrations, No.	Method[a]	Titrant Flow, ml./min.	Corrected[b] Titration Vol., ml.	Measured Molarity	Av. Deviation, %
~0.01 M HCl	1 M NaOH	13	AAB	0.6	1.002	0.01002	0.4
	1 M NaOH	5	AMB	1.4	0.994	0.00994	0.3
	1 M NaOH	5	Wet	. . .	1.007	0.01007	0.9
~0.02 M HCl	1 M NaOH	5	AAB	0.6	1.998	0.01998	0.2
	1 M NaOH	8	AMB	1.3	1.997	0.01997	0.3
	1 M NaOH	5	Wet	. . .	1.992	0.01992	0.3
~0.01 M H$_3$BO$_3$	3 M NaOH	5	AAB	0.6	0.337	0.01011	0.7
	1 M NaOH	5	AMB	2.1	1.018	0.01018	0.7
	1 M NaOH	5	Wet	. . .	0.993	0.00993	0.8
~0.015 M H$_3$BO$_3$	3 M NaOH	9[c]	AAB	0.6	0.506	0.01518	0.5
	1 M NaOH	6[d]	AMB	2.2	1.510	0.01510	0.4
	1 M NaOH	5	Wet	. . .	1.486	0.01486	0.7
~0.005 M H$_3$PO$_4$	3 M NaOH	5	AAB[e]	0.6	0.134[f]	0.00403	1.9
					0.277[g]	0.00416	0.5
	1 M NaOH	5	AMB[h]	1.7	0.829	0.00414	0.5
	1 M NaOH	5	Wet	. . .	0.839[g]	0.00420	0.9
~0.01 M H$_3$PO$_4$	3 M NaOH	5[i]	AAB[e]	0.6	0.274[f]	0.00822	1.3
					0.549[g]	0.00824	0.2
	2 M NaOH	5	AAB[h]	0.6	0.829	0.00829	0.3
	1 M NaOH	5	AMB[h]	1.2	1.676	0.00838	0.2
	1 M NaOH	5	Wet	. . .	1.674[g]	0.00837	0.7
~0.006 M MgCl$_2$	1 M Na$_4$EDTA	5	AMB	1.6	0.656	0.00643	1.6
	1 M Na$_4$EDTA	5	Wet	. . .	0.645	0.00631	0.5
~0.009 M MgCl$_2$	1 M Na$_4$EDTA	5	AMB	1.6	0.976	0.00956	1.0
	1 M Na$_4$EDTA	5	Wet	. . .	0.985	0.00964	0.3
~0.012 M MgCl$_2$	1 M Na$_4$EDTA	5	AMB	1.5	1.302	0.01275	0.5
	1 M Na$_4$EDTA	5	Wet	. . .	1.318	0.01291	0.5

[a] AAB = automatic end point determination; automatic buret. AMB = automatic end point determination; manual buret. Wet = classical volumetric titration; visual end point detection with indicators; same 5-ml. buret as in AMB. [b] Volumes for automatic end point determinations corrected, assuming a lag time of 0.050 min. [c] Two titrations eliminated by Chauvenet's criterion. [d] One titration eliminated by Chauvenet's criterion. [e] Instrument set to detect first two end points. [f] First end point. [g] Second end point. [h] Instrument set to detect only second end point. [i] Instrument did not detect first end point in one titration.

volumetric titrations in which the end points were detected visually with the aid of indicators. The same 5-ml. buret employed in the automatic titrations (manual buret) was used for the classical titrations. The automatic titrations appear satisfactory for routine analyses. The use of a volume correction based on a lag time of 0.05 min. often yielded results less accurate (compared to classical titrations) than the precision would indicate. Thus, in actual control procedures, improvement in accuracy can be obtained by determining the lag time for each particular titration system and instrument setting.

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