A NUMERICAL METHOD FOR TITRATION
END POINT DETERMINATION

MASTER

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DEVELOPMENT DIVISION

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Normal Process Development
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ABSTRACT

A numerical method has been utilized to determine analytically the end point of a potentiometric titration. The method has been programmed for the Wang 700 calculator to aid in the chlorine analysis of TATB. Significant time is saved by using the program because it is no longer necessary to run the entire titration curve and tedious, error-prone graphical techniques of solution are eliminated.

DISCUSSION

A description of the Parr Bomb method of residual Cl^- analysis for TATB has been reported(1). The final step in the analysis is potentiometric titration using a chloride specific ion electrode and AgNO_3 as a titrant. As the volume (V) of titration is increased the resulting voltage (E) is recorded, resulting in an "S" shaped voltage-volume curve. Mathematically, the end point is given as the volume for which the second derivative of voltage with respect to volume is equal to zero. The end point is also the volume for which the first derivative of voltage with respect to volume is a maximum. These figures illustrate the relations between the end point (EP) and the titration curve with its first two derivatives.

The end point is difficult to find on the voltage-volume curve and graphical techniques utilized earlier were found unsatisfactory. If the volume increment of titrant is held constant the derivatives may be calculated by the familiar difference formulas:

$$\left(\frac{dE}{dV}\right)_i = E'_i = \frac{E_{i+1} - E_{i-1}}{V_{i+1} - V_{i-1}} = \frac{E_{i+1} - E_{i-1}}{2\Delta V}$$

$$\left(\frac{d^2E}{dV^2}\right)_i = E''_i = \frac{E'_{i+1} - E'_{i-1}}{V_{i+1} - V_{i-1}} = \frac{E'_{i+1} - E'_{i-1}}{2\Delta V}$$

(1) B. D. Faubion, C. C. Blair, MHSMP-75-20J (January-March 1975).

A program utilizing the finite difference technique has been developed for the Wang 700. Input to the program consists of the titration normality, TATB sample weight, and the constant volume increment to be used. At each step of the titration the typewriter indicates the total amount of titrant added and the corresponding voltage is entered by the user on the keyboard. The numerical derivatives are computed, printed, and checked to determine if the end point has been obtained. The end point has been found if (1) the second derivative is zero and (2) the first derivative is greater than some critical value (usually 1.0). The second condition is necessary because noise in the early part of the titration curve sometimes causes the second derivative to become zero or negative in this region and a false end point would be indicated. The end point has been passed if (1) the second derivative is negative and (2) the first derivative is greater than some critical value. For this case the program uses linear interpolation to solve for the end point. The end point and the percentage Cl^- are printed and the run is complete. Fig. 1 is a sample of the printout from the program.

CONCLUSIONS

Significant time is saved by using the program because (1) it is not necessary to run the entire titration curve and (2) the tedious process of plotting the curve and graphically solving for the end point is eliminated. The numerical methods employed by the program provide an on-line analytical solution for the end point rather than a graphical solution.

SAMPLE NUMBER 3633-XX-001 LOT 2 TELEDYNE

Titration Normality 0.04954
 Sample Weight (g) 0.25024
 Volume Increments (mℓ) 0.10000

<u>Volume (mℓ)</u>	<u>Voltage</u>	<u>First Derivative</u>	<u>Second Derivative</u>
0.00	4.00		
0.10	4.03	0.35000	
0.20	4.07	0.45000	1.00000
0.30	4.12	0.55000	1.00000
0.40	4.18	0.65000	2.25000
0.50	4.25	1.00000	6.75000
0.60	4.38	2.00000	15.50000
0.70	4.65	4.10000	10.00000
0.80	5.20	4.00000	-10.75000
0.90	5.45	1.95000	
1.00	5.59		

End Point (mℓ) 0.74819
 Chlorine (%) 0.52512

Fig. 1. Sample Output from Wang 700 Titration Program