Computer-Controlled Potentiometric Titration System for Rapid Determination of Sulfuric and Organo-Sulfonic Acids in Detergent Intermediates

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ABSTRACT

A potentiometric titration system controlled by a desk-top computer is set up for process control analysis and applied to rapid determination of sulfuric and organo-sulfonic acids in detergent intermediates. The computer takes the weight of sample from an automatic top-loading electronic balance, stores it, controls stepwise additions of titrant, detects two end points, and finally prints out the acid contents in weight per cent. During the titration, the rate of titrant additions is adjusted to electrode response time by frequent monitoring of an electrode potential with the computer. Typical titration time is about 60-70 seconds per sample, and the precision of the determination was satisfactory.

INTRODUCTION

Several potentiometric titration procedures for determining sulfuric and organo-sulfonic acids in detergent intermediates have been described (1,2), as the contents of the acids is a good indication of the quality of the final products. The potentiometric titration methods have subsequently been improved for routine control type analysis (3). However, the potentiometric determination using a commercially available recording type automatic titrator requires ca. 10 min per sample. Therefore, an automatic titration system which permits rapid determination is desired for routine control analysis. This paper describes a computer-controlled potentiometric titration system capable of determining the acid components very rapidly. The computer undertakes all the necessary works such as recording the sample weight, controlling stepwise additions of titrant, detecting the two end points, and printing out the weight per cent of the two acids within 60-70 seconds.

EXPERIMENTAL PROCEDURES

Reagents and Apparatus

Reagents are of analytical grade chemicals. The 0.5 N cyclohexylamine titrant was prepared by diluting a weighed quantity of cyclohexylamine with methanol. The titrant was standardized against sulfamic acid as described previously (3). A top-loading electronic balance (Model PL-200, Mettler, Switzerland) readable to 1 mg with a maximum weighing range of 200 g was used. To ensure an accurate and stable reading of the weight, an air-tight hood was made and mounted on the balance. A pH meter (Model 125, Corning, U.S.A.) with a digital readout and BCD output was used to measure the potential of a glass electrode to 1 mV against Ag/AgCl reference electrode. An automatic piston buret (Model DV-10, Mettler) with an interchangeable 20 ml buret cylinder was used. To control the buret with computer, a slight modification of the electric circuit of the buret controller, Auto Valve 13, was made in this laboratory. The balance, buret, and pH meter were interfaced with a desk-top computer (HP-9825A, Hewlett-Packard, U.S.A.) through the I/O interface (HP-98213A) and BCD Input interface (HP-98033A). The computer program was written in HPL language (a version of BASIC) in this laboratory.

Titration System

A block diagram of the titration system is shown in Figure 1 where the HP-9825A desk-top computer controls commercially available components and performs all the numerical calculations. Before starting a titration, the computer stores a sample weight measured with a top-loading electronic balance linked to the computer. An automatic buret controlled by the computer delivers titrant by driving a stepping motor with a resolution of 2 μl. The titrant is added stepwise and after each addition the electrode potential is provided to the computer through BCD output of a pH meter. The data (volume of titrant, potential) at several titration points are stored for calculating two end points. Upon completion of the titration, weight per cent of the acid components are printed out in a standard form report by a built-in printer.

The computer programs are dimensioned for the statistic evaluation of up to 130 titration results to calculate mean values of the acid contents and the standard deviations. The statistical data can be printed out in a standard form whenever necessary.

Calculations

In the potentiometric titrations described here, two end points appear; the first one corresponds to neutralization of the first replaceable hydrogen of sulfuric acid and organo-sulfonic acid. The second one corresponds to neutralization of bisulfate ion. The two end points were calculated by nonlinear interpolation method described by Keller and Richter (4). A similar method by Wolf (5) was employed when the former method was not applicable under certain conditions. Both methods are the variation of nomograms given by Fortuin (6), using the three largest potential steps and assuming a constant increment of the titrant volume. The first and the second end points thus obtained were used to calculate the acid contents in a sample according to the following equations.

$$\%\ H_2SO_4 = \frac{(V_2 - V_1)N \times 98.08 \times 100}{W} \qquad (I)$$

$$\%\ RSO_3H = \frac{(2V_1 - V_2)N \times MW \times 100}{W} \qquad (II)$$

where V_1, V_2 = milliliters of titrant at the first and the second end points; N = normality of titrant; W = sample weight in milligrams; MW = average molecular weight of organo-sulfonic acid.

Tritrant Additions

In order to reduce a titration time, titrant additions were made stepwise, and only a small number of titration points were measured. The interval of titrant additions was adjusted to the response time of a glass electrode by delivering a new increment of the titrant volume immediately after an electrode equilibrium. The electrode was judged to be

equilibrated when exactly the same potential value was provided three times in succession (for 1.5 seconds) to the computer which reads the electrode potential in every five tenths of a second. As the practical samples from a detergent manufacturing process generally contain a large amount of organo-sulfonic acid and only a few per cent of sulfuric acid, the first end point does not differ from the second end point. Therefore, the titration time was saved by making the first increment volume ΔV_1 large. The optimum size of ΔV_1 was readily calculated as

$$\Delta V_1 = \frac{W}{N \cdot MW} \qquad \text{(III)}$$

based upon the sample weight which was stored prior to the titration. The ΔV_1 is little smaller than V_1, as the molecular weight of organosulfonic acid is about three times larger than that of sulfuric acid. A small size of the equal increment volume of 0.005 ΔV_1 was added stepwise thereafter. The titration was terminated at the third titration point after the second end point where the second derivatives of the titration curve change the sign from negative to positive. Thus, ca. 15-20 sets of data (titrant volumes-potentials) were stored in the computer memory, which were processed in on-line mode to evaluate the first and the second end points.

Titration Procedures

Place a 150 ml beaker which serves as a titration vessel on a weighing pan, press a control bar to tare and take ca. 0.5 g of sample in the beaker. Press a computer key to store the sample weight in the computer memory. Remove the beaker from the weighing pan and add 80 ml of methanol to dissolve the sample completely. The electrodes are immersed into the solution. The sample solution is then titrated with 0.5 N cyclohexylamine while stirring with a magnetic stirrer.

RESULTS

Performance of the titration system was tested by determination repeated on a single sample of detergent

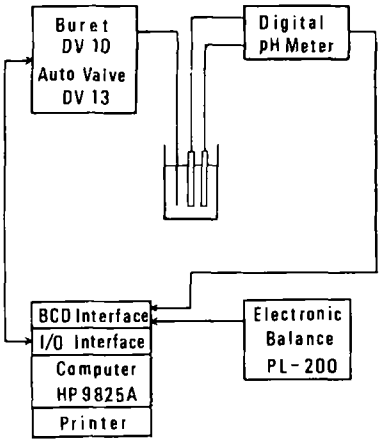

FIG. 1. Block diagram of an automatic titration system, made up of commercially available components.

intermediate. On ten determinations, mean values of 2.24 and 95.4% were realized with relative standard deviations of 0.8 and 0.1% for sulfuric and organo-sulfonic acids, respectively. The time required for a titration was 60-70 seconds, and the acid contents were printed out immediately after the completion of titrant additions. The performance is satisfactory for routine quality control applications in speed, precision, and simplicity.

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