Computer-Controlled Automatic Titration System and Its Application to the Analysis of Fats and Oils

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ABSTRACT AND SUMMARY

An automatic titration system (ATS) controlled by a microcomputer was developed for potentiometric or pH titrations. The titrator is equipped with a piston-type glass buret which is operated by a stepping motor driven by computer-generated pulse. The droplet volume of titrant is 0.00211 ml per pulse which enables very accurate titration. The titration rate is controlled by regulating the intervals of pulses according to the potential changes accompanying the progress of titration. The point giving the maximum pulse interval is detected automatically as the end point. Accordingly, it is not necessary to present the potential or pH value of the end point. Sample beakers are sent in turn with an endless mode. As examples of practical application of ATS, saponification value, amine value, acid value, total chlorine content, and chloride ion content were determined. The ATS makes it possible to contribute not only to the improvement of precision but to the simplification of analytical procedures in fats and oils chemistry.

INTRODUCTION

In the field of fats and oils chemistry, the measurement of saponification value, amine value, acid value, and chloride ion content occupy important positions together with that of other chemical characteristic values. These values are, in most cases, measured using titration procedures. However, manual titration is tedious and precision is difficult.

On the other hand, it has been recognized that the function of a computer is not only to carry out large quantities of calculation and data aquisition but to contribute as one element to support chemical research and to play an essential role for the systematization of research (1). As background, the system, including a group of automatic analytical instruments utilizing a computer, so-called laboratory automation, has been developed, thereby contributing to accurate, efficient, and rapid chemical research. This trend is the same as with volumetric analysis and minicomputer-controlled titrators have been proposed (2,3). A more recent tendency in laboratory automation is to use a microcomputer as a part of analytical instruments.

This paper describes the construction of a microcomputer-aided automatic titration system which has wide applicability in potentiometric or pH titrations. The maximum slope of a titration curve is detected automatically as an end point by a microcomputer. The end point reproducibility was demonstrated in acid-base titration. Other data on practical application to fats and oils chemistry are also presented.

SYSTEM DESIGN

The appearance of the automatic titration system (ATS) is shown in Figure 1 except for the microcomputer and teletypewriter. A general block diagram of ATS is illustrated in Figure 2. The system consists of parts for titration, detection, electrode washing, sample transfer, and control-operation. The functions of each part are described below. A schematic diagram of the titration apparatus is shown in Figure 3.

Titrant Delivery

The function of the titration assembly is to add a titrant dropwise to a sample solution. This part is equipped with a 20-ml piston-type glass buret (Model SB-11, Hirama Sangyo Co., Tokyo, Japan) which is operated by a stepping motor (Model 103-710, Sanyo Electric Co., Tokyo, Japan). The rotation of the stepping motor is converted into an up-and-down motion, by which a glass piston goes up and down in a cylinder to inhale or exhale a titrant. A step-pulse which is generated by a microcomputer (Model LSI-11, Digital Equipment Corp., Maynard, MA) drives a motor by an angle of 1.8°. On the top of the buret, there is an exchange valve which is switched by a motor prior to the motion of the piston. The titrant discharged from the buret is added dropwise to a sample solution through a glass capillary. The output of pulse from the microcomputer is transmitted to the stepping motor through a homemade interface circuit for pulse-voltage conversion. When one titrant is changed to another, the inside of the buret is thoroughly washed by a separately prepared computer program for washing.

Detection Assembly

The detection assembly consists of a combination glass electrode (Model 6015, Electric Chemical Instrument Co., Tokyo, Japan) or a combination Ag-AgCl electrode (Model EA-246, Metrohm, (Herisau, Switzerland) and a digital pH meter (Model HG-2, Electric Chemical Instrument Co., Tokyo, Japan). An electrode potential or pH of a sample solution is transmitted to the microcomputer after conversion into binary code through a homemade interface circuit for code conversion.

Electrode Washing Assembly

The electrode washing assembly consists of an electromotive cylinder, washing bath, and washing liquid tank. Its function is to wash the electrode, glass capillary, and stirring rod. After titration, the electrode is pulled out from the sample solution by an electromotive cylinder and revolved counterclockwise by an angle of 90° to stay above a washing bath. Then the electrode goes down into the washing bath and washing liquid is provided through an electromagnetic valve for the washing liquid tank simultaneously with the rotation of a stirring rod. The washing bath has a double cylindrical structure. Washing liquid flows over from the inside bath to the outside, and is then led to a drainage tank. After washing, the electrode returns to the original position.

Sample Transfer Assembly

This assembly is used to transfer 24 sample beakers on a rectangular sample stand constructed of acrylic resin to the position for titration by employing induction motors which are set up at the four corners of the sample stand. In the sample transfer operation, sample beakers are placed in the holder made by cutting a length of vinyl chloride pipe. The

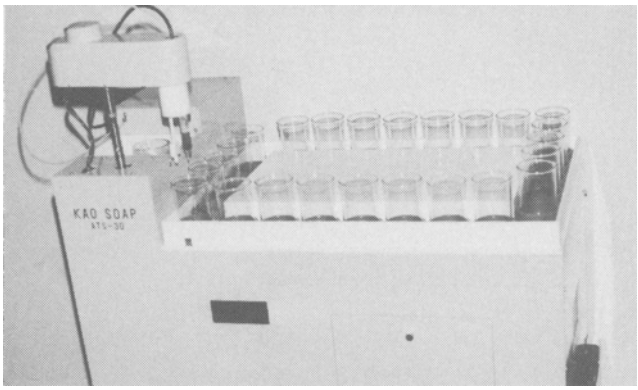

FIG. 1. Appearance of titration apparatus of automatic titration system.

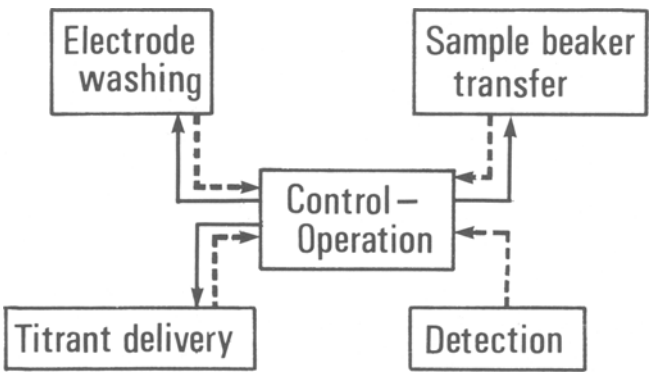

FIG. 2. Functional organization of automatic titration system. Solid line: control signal; dotted line: end point signal.

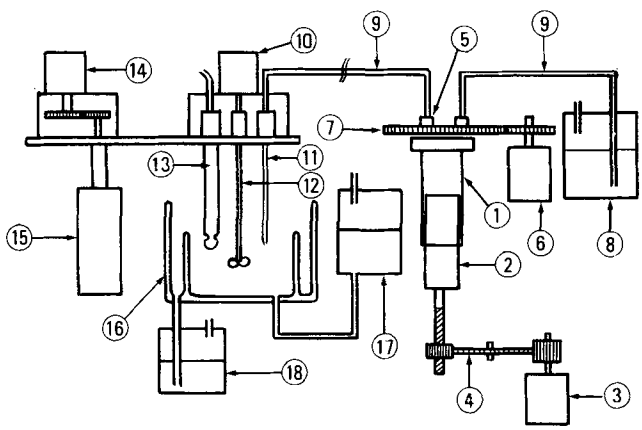

FIG. 3. Schematic diagram of titration apparatus. (A) titrant delivery assembly: 1. cylinder (glass, 20 ml), 2. piston, 3. stepping motor, 4. gear, 5. switching valve, 6. motor for switching valve, 7, gear for switching valve, 8. titrant reservoir, 9. Teflor tube (1.5 mm ID), 10. stirring motor, 11. glass capillary, 12. stirring rod; (B) detection assembly: 13. combination electrode; (C) electrode washing assembly: 14. motor for rotating titration part, 15. electromotive cylinder, 16, washing bath, 17. washing liquid tank, 18. drainage tank.

holders are sent in turn with an endless mode. The sample stand is euqipped with an acrylic resin cover, and it is possible to perform a titration in an atmosphere of nitrogen.

Control-Operation Assembly

A microcomputer was used for hardware control (electrode washing, motion of the electrode, and sample beaker transfer) and for software control (control of addition rate of titrant, detection of end point and calculation of analytical values) .

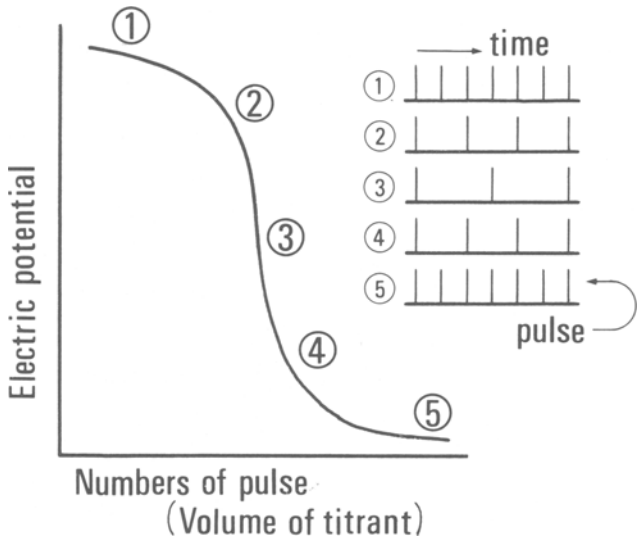

FIG. 4. Typical titration curve and pulse interval.

Addition rate is adjusted by a fine rotation of a stepping motor. The stepping motor is driven with the computer-generated pulses depending upon the increment of electrode potential during titration. Accordingly, at the early stage of titration as shown in region 1 of Figure 4, the intervals between pulses are very short because the potential changes slowly. Therefore, a titrant is added with a fast addition rate. As the end point is approached, the pulse intervals become longer in proportion to the potential change thereby decreasing the addition rate gradually. Thus, the titrant is added very slowly in the neighborhood of the end point. After the end point, the addition rate again increases gradually up to the initially specified potential at which titration is completed. The point giving the maximum pulse interval is detected automatically as the end point and then the calculated analytical result is printed out by a teletypewriter.

All programs used in this system were written in an assembly language of about 4 kilowords including the program for washing.

EXPERIMENTAL PROCEDURES

Reagent

0.5 N. alcoholic potassium hydroxide solution: In 140 ml of deionized water, 111 g of reagent grade potassium hydroxide were dissolved and diluted to 3 liters with ethanol. After 3 days, the solution was filtered.

0.1 N perchloric acid solution: A mixed solution of 114 g of reagent grade acetic anhydride and 50.1 g of reagent grade perchloric acid (60%) diluted with acetic acid to 3 liters was stored in a brown reagent bottle as a titrant for amine. The titrant was standardized against anhydrous sodium carbonate using the ATS.

Acetic anhydride-acetic acid mixed solution: Acetic anhydride and acetic acid were mixed as a ratio of 9:1.

Sample: All samples used for this study were manufactured or synthesized by our company.

Procedures

Saponification value: The material to be examined was heated with a measured excess of alcoholic potassium hydroxide until completely saponified. After saponification the sample beaker was covered with Parafilm membrane (PARAFILM®, American Can Co., Greenwich, CT) and then nitrogen gas was passed through the apparatus. The

excess potassium hydroxide was titrated with a hydrochloric acid standard solution in an atmosphere of nitrogen. The saponification value was calculated and was typed out by a teletypewriter.

Amine value: Total amine value is obtained by titrating primary, secondary, and tertiary amines in acetic acid with perchloric acid. Tertiary amine value can be given by acetylation of primary and secondary amines with an acetic anhydride-acetic acid mixed solution followed by titration of unreacted tertiary amine with perchloric acid. The volume of perchloric acid added was converted to the corresponding milligrams of potassium hydroxide.

Acid value: A weighed sample dissolved in ethanol was titrated with potassium hydroxide which was standardized against sulfamic acid.

Total chlorine content: A sample to be measured was heated with n-butanol and metallic sodium for 1.5 hr on a sand bath until completely decomposed. After cooling, deionized water and nitric acid were added to the solution which was titrated with a silver nitrate standard solution.

Chloride ion content: The content was obtained by dissolving a sample in deionized water acidified with nitric acid followed by titration with a silver nitrate solution.

RESULTS

Calibration of Buret

The volume of titrant added to an end point is calculated from total pulse numbers generated up to the end point. Accordingly, the volume of titrant per pulse was calculated from the weight of redistilled water exhaled for given pulse numbers. The titrant volume per pulse was found to be 0.00211 ml. The small coefficient of variation, 0.024%, is obtained only by ATS. This is one of the remarkable characteristics of the ATS using a microcomputer.

TABLE I

Comparison of Saponification Values

Sample	ATS[a]			Manual[b]		
	SV[c]	Runs	CV (%)[c]	SV[c]	Runs	CV (%)[d]
Oleic acid	204.6	9	0.15	204.1	5	0.30
Ester (1)	250.7	5	0.11	250.0	4	0.14
Ester (2)	223.1	4	0.12	225.1	4	0.26
Ester (3)	253.5	5	0.16	255.4	5	0.20
Polyester	556.0	9	0.17	556.0	4	0.45

[a]ATS = automatic titration system.
[b]Indicator titration method using phenolphthalein.
[c]SV = saponification value.
[d]CV = coefficient of variation.

Precision of Acid-Base Titration

Repeatability in the titration of hydrochloric acid with 0.1 N potassium hydroxide was examined. The coefficient of variation (10 repeated runs) was 0.045% while it was 0.070% in manual titration using phenolphthalein indicator. Thus, the precision of titration by ATS is better than a conventional manual method.

Coefficients of variation in sampling of distilled water using a 20-ml volumetric pipet and a 20-ml automatic pipet were 0.035% and 0.042%, respectively. The precision of titration obtained from the above experiment was almost equal to that of sampling by a pipet.

In acidimetry, basic sample solutions may absorb carbon dioxide in the air while a sample solution is allowed to stand before titration or during the titration which causes an error. The preliminary examination showed that this problem was solved by covering the titration beakers with Parafilm membrane immediately after sampling and by dis-

TABLE II

Comparison of Total Amine Values

Sample	ATS[a]			Manual[b]		
	TAmV[c]	Runs	CV (%)[d]	TAmV[c]	Runs	CV (%)[d]
Dodecyldiethanolamine	198.2	5	0.14	197.5	5	0.28
Dodecylamine	292.4	6	0.15	292.5	3	0.24
Dodecylmethylamine	262.7	5	0.13	262.0	3	2.53
Dioctylamine	221.5	5	0.17	222.1	3	0.55

[a]ATS = automatic tetration system.
[b]Amine values were calculated from titration curves recorded by an automatic potentiograph.
[c]TAmV = total amine value.
[d]CV = coefficient of variation.

TABLE III

Comparison of Tertiary Amine Values

Sample	ATS[a]			Manual[b]		
	Tert AmV[c]	Runs	CV (%)[d]	Tert AmV[c]	Runs	CV (%)[c]
Dodecyldiethanolamine	197.4	10	0.10	196.5	10	0.22
Oleyldiethanolamine	147.8	6	0.09	150.3	3	0.72
Trioctylamine	153.9	6	0.13	154.8	3	0.13
Methyldioctadecylamine	99.8	6	0.11	101.5	3	0.28
Dimethyldodecylamine	252.6	6	0.07	253.3	3	0.45
N-Phenyldiethanolamine	306.6	5	0.19	305.3	3	0.05
N-Methylmorpholine	551.0	6	0.13	548.4	3	0.14
Polyamine	0.21	6	1.73	0.24	3	6.45

[a]ATS = automatic titration system.
[b]Amine values were calculated from titration curves recorded by an automatic potentiograph.
[c]Tert AmV = tertiary amine value.
[d]CV = coefficient of variation.

TABLE IV

Comparison of Acid Values

Sample	ATS[a] AV[c]	ATS[a] CV (%)[d]	Manual[b] AV[c]	Manual[b] CV (%)[d]
Oleic acid	198.2	0.06	198.7	0.16
Lauric acid	277.8	0.06	276.6	0.64
Myristic acid	244.7	0.08	244.0	0.37
Mixed fatty acid[e]	211.5	0.04	210.8	0.23
Blended oleic acid[f]	40.6	0.17	40.5	0.24
Blended oleic acid[f]	10.3	0.39	10.5	0.55
Blended oleic acid[f]	0.12	1.32	0.14	4.22

[a]ATS = automatic titration system.

[b]Indicator titration method using phenolphthalein.

[c]AV = avid value.

[d]CV = coefficient of variation.

[e]Fatty acid consisting of carbon numbers of 8 to 18.

[f]Oleic acid blended with dioctylphthalate.

placing air with nitrogen gas.

As a model of acidimetry, the titration of potassium hydroxide with hydrochloric acid was studied. An alkaline aqueous solution and an alcoholic solution were used as sample solutions. The coefficients of variation (10 repeated runs) were 0.034% and 0.032%, respectively. It is obvious that titrations were carried out with good precision both in aqueous or alcoholic solutions.

Practical Application of ATS

As an example of practical application of ATS, saponification values, amine values, acid values, total chlorine contents, and chloride ion contents were determined.

The repeatability of saponification value was examined using dioctylphthalate as a standard. Mean values of duplicates were 288.0 and 288.4 (CV = 0.16% and 0.11%), respectively (10 repeated runs). On the other hand, the mean values obtained by manual titration using phenolphthalein and by reading the end point of the titration curve recorded by a potentiometric titrator (Model E-436, Metrohm) were 287.3 and 287.5 (CV = 0.13% and 0.31%), respectively. The precision by the ATS was comparable to that by conventional manual method. Another example is shown in Table I where ATS method and manual titration method using phenolphthalein were compared for fatty acid and various esters. The agreement between saponification values by both methods was satisfacctory, and in most cases the ATS method gave the smaller coefficient of variation.

The total and tertiary amine values by ATS and a conventional manual indicator titration method were listed in Tables II and III. ATS gave an equal or smaller coefficient

TABLE V

Comparison of Total Chlorine Content and Chloride Ion Content

Sample	ATS[a] Cl %	ATS[a] CV (%)[b]	Manual Cl %
Total chlorine content			
Dimethyldodecylamine	0.13	4.33	0.13
Dodecylbetain	5.09	0.34	5.03
Dodecylchloride	17.13	0.25	17.23
Dioctylether	1.88	0.31	1.89
Chloride ion content			
Dodecylbetaine	4.95	0.10	4.92
α-olefin sulfonate	0.34	0.05	0.33
Polyoxyethylene dodecylether sulfate	2.35	0.25	2.33
Sodium chloride	60.47	0.09	60.44

[a]ATS = automatic titration system.

[b]CV = coefficient of variation.

of variation in total and tertiary amine value measurements. In the measurement of amine values, it is important to choose a suitable final electrode potential for the ATS since amine shows a different potential change depending upon its basicity. From preliminary investigation the magnitude of potential change around the end point was found as follows: aliphatic amines and ethoxylated amines, 300-350 mV; aromatic amines and polyamines, 150-200 mV; diamines, 100-150 mV.

Table IV shows the acid values by ATS and a manual titration method. The ATS method is capable of greater precision that the conventional manual method.

The total chlorine content and chloride ion content by ATS and manual potentiometric method were listed in Table V. These data show that the ATS makes it possible to measure automatically the characteristic values in fats and oils chemistry with satisfactory precision and accuracy.

The total time required to analyze one sample by using ATS is 4.5 to 5 min, including the time for titration, electrode washing, sample transfer, and output of the result.

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