Coulometric Determination of Organic Acids[1]

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Abstract

A system has been devised for the coulometric titration of organic acids in a non-aqueous medium. The solvent system is benzene-methanol, 1:1, containing LiCl as the electrolyte. The acid is titrated by reducing hydrogen ion at a platinum cathode. The anode reaction involves the formation of AgCl on silver. The endpoint is detected by an antimony-glass electrode pair and the derivative of the electrode output is used to effect automatic current shut-off. Alternative reference electrodes are discussed. Usual sample size titrated is 0.01 meq but the method can be applied to both larger and smaller amounts.

The method has been applied to the determination of acid value and free fatty acid in fatty materials. The advantages of the coulometric determination are: 1) No standard solutions are required. 2) The titration is conducted without analyst attention. 3) The technique is simple and rapid.

Introduction

THE DETERMINATION of acid value of fatty acids, fats, various processed fatty materials, and other organic compounds is one of the more frequent analyses conducted in the analytical laboratory. Although little difficulty is encountered in the standard titrimetric determination, on occasion highly colored samples are encountered which obscure the visual endpoints; and, particularly for the titration of small amounts of organic acids, the preparation and maintenance of standard alkali titrants is bothersome.

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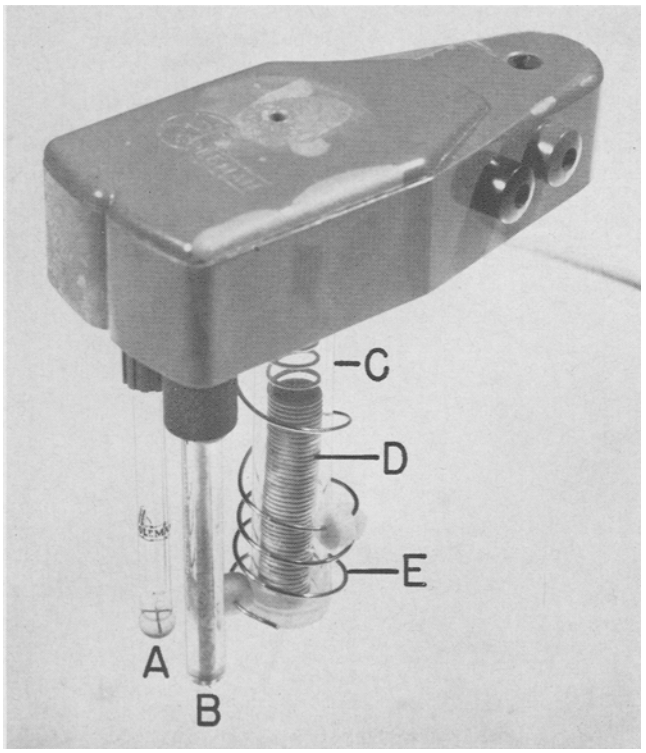

FIG. 1. Generator-detector head for coulometric titrator: A. glass electrode; B. antimony electrode; C. porous Vycor anolyte cell; D. silver anode; E. platinum cathode.

The work done by Taylor and Smith (1) at the National Bureau of Standards on the coulometric titration of acids and bases in aqueous systems encouraged us to extend this technique to the determination of organic acids in non-aqueous solvents. In the coulometric technique, the sample is titrated by electrically generated reagent in an electrolysis cell. The amt of titrant is calculated from the magnitude of the electrolysis current and the elapsed time. Use of an electrometric endpoint to control titrant generation also makes possible the development of a completely automatic apparatus.

While an increasing number of papers on coulometry are appearing in the literature, very little has been reported on coulometry in non-aqueous systems (2,3,4,5).

Experimental

The Coulometric Titration. For the titration of acids alone or as minor constituents of tallows or other fats, a non-aqueous solvent system is required since fats will not dissolve appreciably at room temp if as little as 5% water is present. Fritz and Lesicki (6) have reported that a benzene-methanol mixture serves as a suitable solvent for the volumetric titration of carboxylic acids. According to the Lewis theory, the methanol, an amphiprotic solvent, assumes a role similar to water in the neutralization reaction in the non-aqueous medium. A 1:1 benzene-methanol mixture was found to have the necessary solvent properties for the various fat samples.

The titrant is generated in a manner similar to that used by Taylor and Smith (1). Lithium chloride is used as the supporting electrolyte. A silver anode is used and, at the anode, silver is oxidized to silver ion which is removed from solution by the formation of insoluble silver chloride, releasing an electron for the neutralization reaction. At the platinum cathode, hydrogen ion is reduced to hydrogen. The electrode reactions are:

$$\text{Anode:} \quad Ag + Cl^- \longrightarrow \underline{AgCl} + e$$

$$\text{Cathode:} \quad H^+ + e \longrightarrow 1/2H_2\uparrow$$

$$\text{Cell:} \quad H^+ + Cl^- + Ag \longrightarrow \underline{AgCl} + 1/2H_2\uparrow$$

Lithium chloride was selected as the electrolyte because of its solubility in the solvent medium.

The electrolysis cell (Fig. 1) consists of a silver anode inside a porous Vycor chamber around which is a spiral wound platinum cathode. The porous Vycor permits electrolytic contact but prevents the silver chloride precipitate from reaching the platinum cathode and participating in the cathode reaction.

Endpoint Detection. The neutralization reaction is followed and the endpoint detected by an antimony-glass electrode pair arranged as shown in Figure 1. The generating-detecting head is a modified Coleman pH electrode holder. The indicating electrode is a Coleman Hyalk glass electrode and the antimony reference electrode was made in this laboratory. The use of a high alkaline-glass electrode was suggested by the work of Van der Heijde and Dahmen (7). High alkaline-glass electrodes are superior to ordinary glass in non-aqueous systems as demonstrated in this and other laboratories, however, no reason can be found in the literature for this obvious superiority. High alkaline-glass electrodes are generally constructed of

lithium glass and it is speculated that the ionic mobility of the hydrogen ion across the solution-glass interface and through the glass is responsible in some way for this behavior.

Two other reference electrodes were paired with the glass electrode and evaluated in the detector circuit. A standard calomel reference and a silver-silver chloride reference gave good results and essentially the same potential change before and after titration. The antimony reference gave slightly less potential difference but eliminated a six sec response lag that occurred with the other two probably due to liquid junction equilibrium effects. The antimony reference also eliminated the drift and malfunction which sometimes occurred when the fiber or ground-glass junctions became dehydrated in the benzene methanol electrolyte.

Titration curves obtained with this generator-detector assembly are shown in Figure 2. A Coleman line-operated pH meter connected to a recorder adjusted to 200 mv full-scale deflection was used for the recordings.

The stoichiometric endpoint of the titration was found to be that point on the titration curve where a line drawn at 45 degrees from the horizontal becomes tangent to the curve. This is slightly beyond the point of inflection usually taken as the endpoint. Previous work with continuous titrations has proven the value of titrating to a reproducible excess of titrant, particularly when the reaction is suspected of being non-instantaneous. The difference in titration times for the samples and blank measured to these points gave a calculated current efficiency of 100%. The tangents and associated endpoints are indicated in Figure 2.

Automatic Titration. The procedure outlined above for determining the endpoint, though satisfactory, is quite time consuming. Since the endpoint occurs at the same value of slope each time regardless of the absolute value of the electrode potential, it was decided to differentiate the curve and select the endpoint from the absolute value of slope or curvature. An electronic differentiator was constructed for this purpose which employs a Philbrick solid-state operational amplifier of the type used in analog computers. Design of the differentiator was supplied by Philbrick Associates. Two typical titration curves and their electronic derivatives are presented in Figure 3.

In this figure, the ordinate is in units of recorder deflection. The potentiometric curve is obtained in units of mv and sec, but the derivative curve is the instantaneous rate of change of the titration curve in units of mv per sec on the ordinate and sec on the abscissa. The complex shape of the derivative curve is the result of several causes. First, the electronic derivative shown here deviates from the true mathematical derivative during the first few sec of the titration because it starts from zero rather than at a finite value. Secondly, the double max observed in the derivative curve is real and reflects truly the rate-of-change of the potentiometric curve which has a slight inflexion in the rising portion. This behavior may be due to the inherent non-linearity in the electrode response, but is more likely caused by the titration of some impurity in the methanol solvent. Since a blank is used, this behavior causes no difficulty in the analysis.

Use of a first derivative endpoint detection device is unique in that it senses the slope of the titration curve

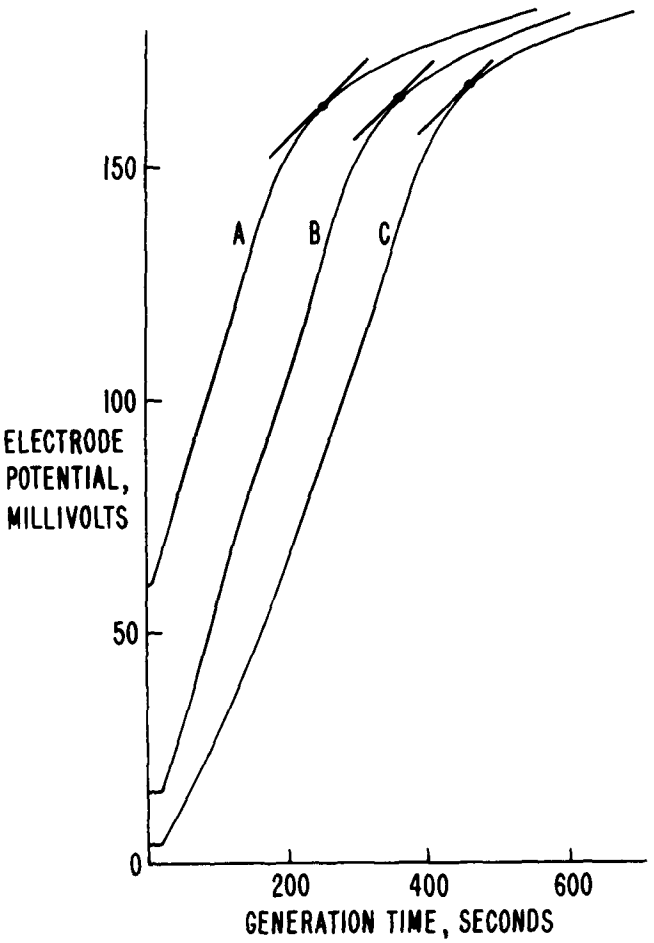

FIG. 2. Coulometric titration curves of: A. reagent blank; B. 0.01 meq stearic acid; C. 0.02 meq sebacic acid. Ten ma generation current.

and not its absolute value. It is not necessary, therefore, to preselect a mv endpoint, but only to determine, once, the shape of the titration curve and the position of the endpoint on the curve.

An automatic titrator was constructed in which the output signal from the differentiator is used to

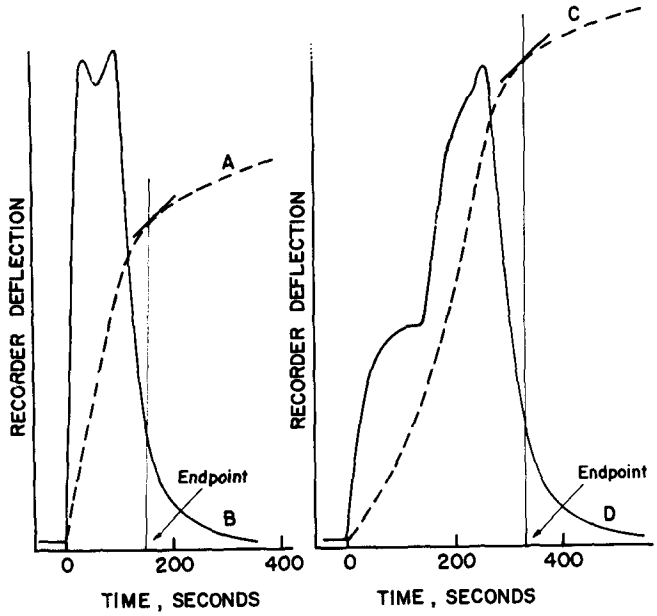

FIG. 3. Comparison of titration curves and corresponding electronic derivatives: A. blank reagent titration curve; B. electronic derivative; C. titration curve of 0.01 meq oleic acid; D. electronic derivative. Ten ma generation current.

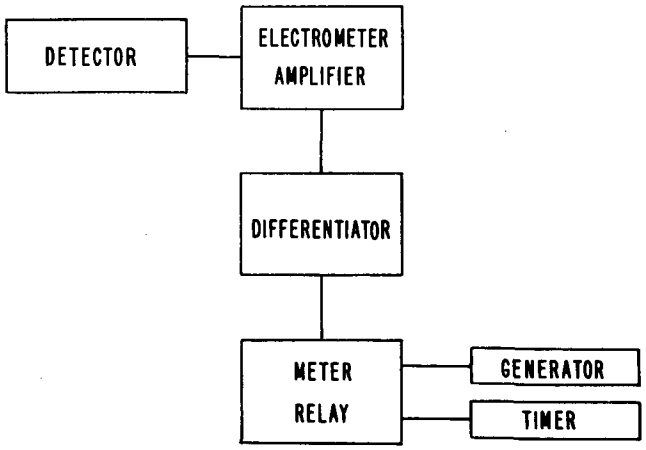

FIG. 4. Block diagram of automatic, coulometric titrator.

activate a meter relay. The meter relay is designed to make electrical contact at a preselected position on a descending motion of the pointer. When a signal corresponding to the differential curve of Figure 3 is impressed on the meter the pointer, starting at zero, swings up scale to a max value which is the peak of the curve after which it moves down scale until it makes contact at a preselected value corresponding to the desired slope or curvature. This meter relay in turn shuts off the generator and timer. A block diagram of the total instrument is presented in Figure 4. A schematic diagram is presented in Figure 5.

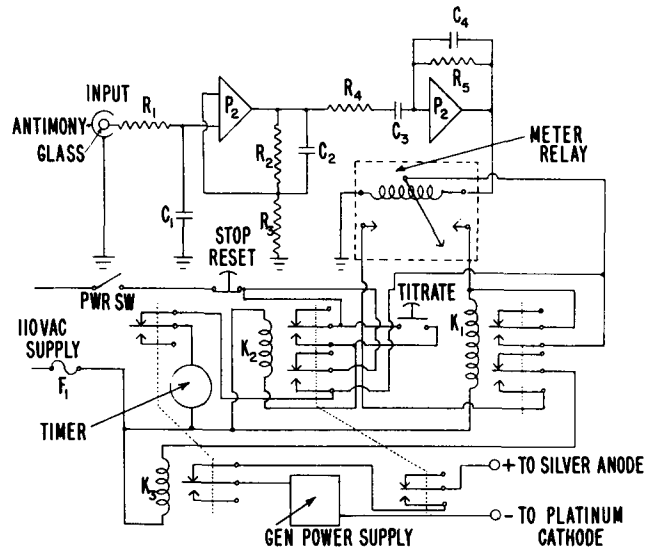

FIG. 5. Schematic diagram of automatic coulometric titrator.

R_1	2 meg ohm	½ watt
R_2	1 meg ohm	½ watt
R_3	10,000 ohm	½ watt
R_4	10,000 ohm	½ watt
R_5	1 meg ohm	½ watt
C_1	.005 micro-farad—silver mica	
C_2	1.001 micro-farad—(1 mfd and .001 mfd in parallel)	
C_3	1.0 micro-farad—200 V	
C_4	0.01 micro-farad—200 V	
K_1, K_3	D.P.D.T. Relay—115VAC Coil—Potter-Brumfield Type KA-11AY	
K_2	3.P.D.T. Relay—115VAC Coil—Potter-Brumfield Type KA-14AY	
S_1	S.P.S.T. Toggle switch	
Timer	Cramer controls type 633E (Cramer Controls Centerbrook)	
P-2	Philbrick Operational Amplifier	
Meter	Assembly Products Continuous Reading Meter Relay Model 451 CR, 0–20 uA	
F_1	3 AMP fuse	
Stop Reset	Push button switch—normally closed	
Titrate	Push button switch—normally open	

Generator Power Supply—Any D.C. constant current supply capable of supplying well regulated current @ 10 ma (a 22.5 v batt. equiv. to Eveready #768 with a 2000 ohm resistor in series with one side is acceptable).

TABLE I

Comparison of Known and Determined Amounts of Fatty Acid

Fatty acid	No. detns.	Taken		Found	
		Meq	Mg	Meq	Recovery
					%
Oleic	2	0.0103	2.91	0.0104 ± 0.0003	100.9
Oleic	3	0.0206	5.82	0.0200 ± 0.0006	97.1
Stearic	2	0.0104	2.96	0.0104 ± 0.0003	100.0
Stearic	3	0.0208	5.92	0.0207 ± 0.0003	99.5
Sebacic	2	0.0103	1.04	0.0106 ± 0.0004	102.9
Sebacic	2	0.0206	2.08	0.0206 ± 0.0000	100.0
σ	(n = 14)	.....	.....	0.0003	.....
Coefficient of variation	.....	.....	.....	2%	.....

Procedure. To perform an analysis with the automatic titrator, weigh a sample containing approximately 0.01 meq of fatty acid (2.8 mg for oleic) into a 150-ml beaker. Add 100 ml of 1:1 benzene-methanol solvent containing 0.75 N LiCl. If more convenient a larger sample can be dissolved in the solvent and an aliquot used for the analysis. The benzene and LiCl should be reagent grade, and the methanol, spectroscopic grade. Reagent grade methanol gave a blank titration almost double that of the spectroscopic grade. Lower the generator and detector electrodes into the beaker and start the magnetic stirrer. After a 30-sec pause to allow the detector electrodes to stabilize, depress the "titrate" button. This energizes the generator electrodes and starts the timer. The titration proceeds until the m relay reaches the preselected value of slope: then contact is made and the generator and timer stop. Using the current in ma (I) and time in sec (t), calculate the number of meq (M) titrated,

$$M = It/96{,}493$$

$$\% \text{ fatty acid} = \frac{M \times \text{equivalent wt}}{\text{mg sample}} \times 100$$

Application. Using this procedure, a series of analyses were performed on oleic, stearic, and sebacic acids. The results are reported in Table I.

The coulometric results indicate a standard deviation of 0.003 meq in the range of 0.01 to 0.02 meq, or a coefficient of variation of about 2% on fatty acid samples. Satisfactory results are obtained on both mono- and dibasic acids and, as expected, no difference between the two acid groups in sebacic acid is observed.

The coulometric method was applied to some typical laboratory samples containing low amounts of free fatty acid. Results are indicated in Table II.

It can be concluded from these results that the coulometric method has a precision equal to that of the AOCS titrimetric method and that the results contain no bias.

Discussion

The primary advantage of the technique outlined above is in its ability to determine accurately small amounts of fatty acid. Besides its application to the determination of acid value and free fatty acid, it is possible to titrate paper chromatographic fractions and major gas chromatographic fractions with high precision. The coulometric procedure is the preferred technique when less than 10 mg of sample is available for analysis; such is often the case with biological samples. A further advantage is the fact that this technique eliminates the need for standardized reagents. This is particularly important at a micro level because it is difficult to make, maintain, and use

dilute analytical reagents in the thousandth normal range. This method can replace the usual alkali titration with phenolphthalein on highly colored fat samples such as soap stock where visual end point detection is difficult or impossible. Additional suggested applications include the determination of hydroxyl value, carbonyl value, and other methods where a titration of acid is required. The titration of acids in aqueous media has been described by Taylor and Smith (1) and could be accomplished automatically with the same equipment as that described in this report.

Further improvements in precision can be effected by the use of purified or neutralized methanol in the solvent system. The resulting reduction in the blank and sample titration times, particularly for smaller samples, would improve precision of the "Titration-Blank" calculation. The method can be extended to even smaller samples, perhaps to less than 0.1 mg. of fatty acid, by reducing the electrolysis rate and sample volume with only a small increase in standard deviation. The ultimate limit of detection of the method is controlled by the solubility of silver chloride in the electrolyte solution.

The work reported here is part of a program now underway in our laboratories to examine the many aspects of coulometry and of amperometric and potentiometric end point detection.

TABLE II
Determination of Free Fatty Acid

Sample	% FFA as oleic				Difference
	Detn.	AOCS	Detn.	Coulometric	
					%
Tallow	1	1.67	2	1.62 ± .05	+0.05
Tallow	1	2.61	1	2.67	−0.06
HAVF	1	41.42	1	41.40	+0.02
Soybean	....	.....	....	.....	.....
Acidulated Foots	2	59.73 ± .24	2	59.25 ± 1.05	+0.48

Acknowledgment

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Defatted Peanuts: Preliminary Cost Study[1]

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Abstract

Defatted peanuts are high in protein and low in fat content. A preliminary cost study for defatting Virginia peanuts with hexane in three all-new hypothetical commercial plants indicates operating cost can be as low as 84 cents/lb of peanuts extracted when packaged in 502 x 308 tins. Cost in fully depreciated plants is as low as 61.5 cents for a volume of extracted peanuts equivalent to the amount of unextracted peanuts normally packaged in 502 x 308 tins. Process development shows promise for further reducing these costs which are based on limited exploratory pilot plant research.

Introduction

DEFATTED PEANUTS were first investigated by Willich and Feuge (1). This early work established general conditions of extraction, which were later used in the pilot plant at the Southern Regional Research Laboratory (2). Limited pilot plant research has established a basis of operation for producing a product having acceptable taste and appearance. It is expected that a quality product would appeal to those desiring lower-calorie diets. In addition, peanut meal prepared by extracting lightly roasted peanuts with hexane is already being included in the diet of hemophiliacs to obtain relief from bleeding (3).

This report describes a hypothetical commercial plant including processing, recovery, packaging, and storage facilities.

Process

The process is shown in Figure 1, and a material balance is given in Figure 2. It is a batch process consisting chiefly of extraction, desolventizing, salting, drying, and packaging. Fully roasted, shelled medium Virginia peanut kernels are extracted at ambient temp with commercial hexane in a battery of 5 extractors for 120 hr (5 days), for removal of 80% of the fat naturally occurring in them. The oil is recovered under 24" to 27" Hg. vacuum in a high-velocity, rising-film evaporator, and the solvent removed is condensed and reused. The extracted peanut kernels containing 35% solvent by wt are then desolventized in a forced draft dryer at 150F for 4½ hr and at 212F for an additional 6½ hr. An alternative to this is desolventization at 212F and 27" Hg. vacuum for 9 hr. Solvent removed is condensed and returned to solvent storage. The desolventized peanuts are salted on an oscillating feeder where they, on being sprayed, absorb 20% by wt of water. After this they are sprinkled with salt amounting to 10% of their dry defatted wt. The wet, salted, defatted peanut kernels are then dried in a forced draft dryer for 8 hr at 150F, vacuum and gas packed in a nitrogen atmosphere containing less than 2% oxygen in 502 x 308 tins, better known as the 1-lb coffee can, and packaged 12 cans to the case.

Plant

Three all-new hypothetical plants were studied. In the small plant each extractor has a capacity for 200 lb of unextracted peanut kernels; in the medium plant for 400 lb; and in the large plant for 600 lb. Operating 250 days, 24 hr per day, total annual processing rates are 50,000, 100,000, and 150,000 lb of unextracted peanuts, yielding 28,500, 57,000, and 85,500 lb of defatted peanuts, respectively.

The hypothetical plants include storage facilities, process and packaging equipment, piping, instrumen-

[1] Presented at the Peanut Utilization Research Conference, Jan. 15–16, 1962, New Orleans, La.
[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.