An Automated Method for Determining Free Alkalinity or Acidity in Soap

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Abstract

An AutoAnalyzer method has been developed to determine free alkalinity or acidity in soap by use of a mixed cresol red-phenolphthalein indicator solution and by measurement of the color developed at 550 mμ. An internal standard or reference solution is used consisting of a soap solution which has been adjusted to represent neutrality. The method was applied for 0 to 0.10% free alkalinity, calculated as sodium hydroxide, and for 0 to 0.50% free acidity calculated as oleic acid. Attainable precision of the method (95% confidence limits) in the ranges explored was found to be ±0.0025% for free alkali and ±0.05% for free acidity.

Introduction

AN EARLIER PAPER (1) described the use of the AutoAnalyzer for the determination of hexachlorophene in soap. In this paper we report the application of the AutoAnalyzer in determining the free alkalinity or acidity in soap.

The usual soap-making procedure leaves a slight excess of alkalinity, usually 0.04% or lower. Accurate determination of free alkalinity in soap has always been a controversial subject. No one method has been universally accepted for scientifically accurate results. Cox (2) precipitated the soap with barium chloride and then titrated the free alkali. Others have salted out the soap with sodium chloride (3). Biffen (4) used neutral alcohol but centrifuged instead of filtering. Uhlig and Duemmling (5) used a solvent mixture of benzene, alcohol, and water. The procedure most commonly employed is that of AOCS Official Method Da 4a-48. This method consists of dissolving the soap in neutralized, boiled alcohol, removing any insoluble matter by filtration, and titrating the hot filtrate to the phenolphthalein end-point with 0.1N HCl. This method is generally accepted as giving reasonably accurate results for practical purposes.

We have found that measurement of the color developed by a mixed cresol red-phenolphthalein indicator in a 5% solution of soap in 50% alcohol can give meaningful and reproducible results for both free alkalinity and acidity when used under the controlled conditions provided by the AutoAnalyzer.

Experimental Section

Equipment

AutoAnalyzer (Technicon Controls Inc.) with following components: Sampler II; proportioning pump (2-speed); colorimeter, Model 1, with 15-mm flow cell, 550-mμ filter, and No. 6 aperture; recorder (single pen); pump and transmission tubing, connectors, and coils.

Regular laboratory equipment as required

Reagents

50% alcohol (SDA 3A diluted with distilled water)
0.1% cresol red (o-cresolsulfonphthalein) in alcohol
1.0% phenolphthalein in alcohol (sufficient NaOH added to make slightly pink)
20 ml of 0.1% cresol red plus 75 ml of 1.0% phenolphthalein plus 95 ml of distilled water made up to 1 liter with 50% alcohol

Procedure

AutoAnalyzer Set-up (Fig. 1). Sample at 2.02, air at 0.80, and indicator at 2.42 cc/min are pumped and joined together into one stream by means of a G-1 cactus connector. (Solvaflex tubing is used except for the air.) The solution is passed through three small mixing coils (Technicon No. 105–88) and to the colorimeter, which is equipped with a 550-mμ filter, No. 6 aperture, and a 15-mm flow cell. A tube at 2.89 cc/min pumps from the flow cell to the drain. Air bubbles and excess liquid are expelled by the overflow from a debubbler installed just ahead of the colorimeter flow cell.

Preparation of Reference Solutions. Obtain a sample of soap and determine the free alkalinity or acidity by AOCS Official Method Da 4a-48. In the case of colored soaps, the greatest accuracy is achieved by using a reference solution of the same color as the samples to be analyzed. Prepare a 5.0% solution of the soap (soaps) in 50% alcohol, including sufficient standard acid or alkali just to neutralize what was found by the AOCS method. Filter if cloudy.

Preparation of Samples. Weigh 5.0 g of sample, dissolve in 50 to 75 ml of 50% alcohol on a steam bath, transfer to a 100-ml volumetric flask, cool to room temperature, and make up to volume with 50% alcohol. Filter if cloudy.

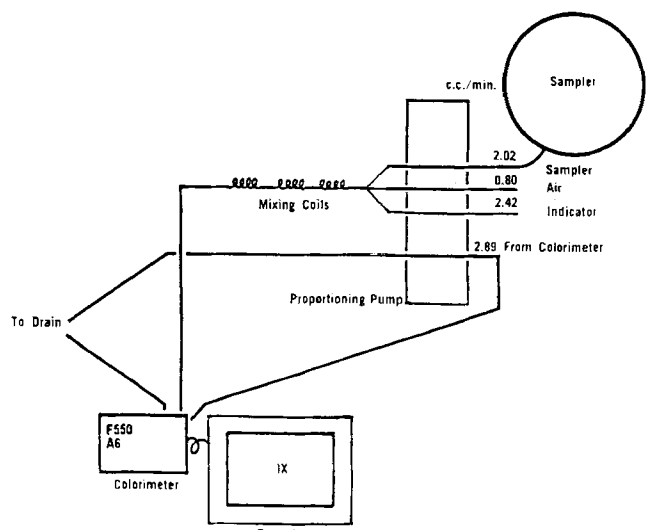

FIG. 1. AutoAnalyzer method for free alkalinity or acidity in soap.

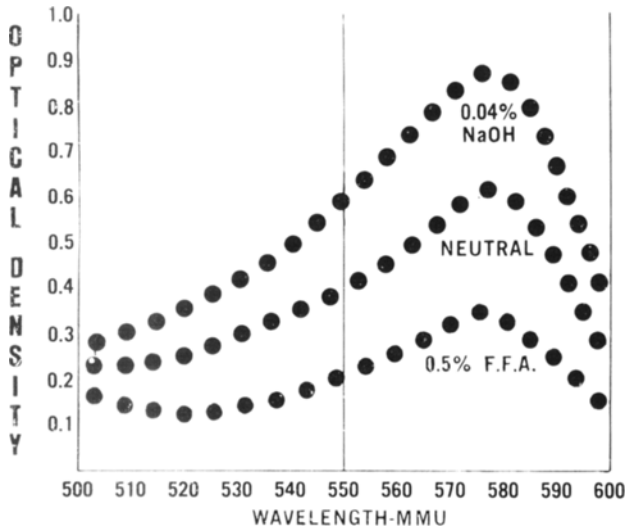

FIG. 2. Sensitivity to free alkalinity or acidity.

Determination of Free Alkalinity or Acidity. Start the AutoAnalyzer system pumping indicator, air, and 50% alcohol (sample tube). Run until the recorder chart baseline is even, then set it at zero absorbance. Load the sampler as follows: fill alternate sample cups with samples, or reference solution (one reference solution for each four samples). Fill the other cups with solvent (50% alcohol).

Operate the sampler at speed 50–2/1. Record optical densities from recorder chart. Calculations follow:

$$\frac{\text{Optical density of sample}}{\text{Optical density of reference solution}} = F$$

For $F \geqslant 1.00$:

$$\% \text{ free NaOH} = 0.08\ (F - 1.00)$$

For $1.00 > F \geqslant 0.55$:

$$\% \text{ free acidity (as oleic)} = -1.08F + 1.06$$

Results and Discussion

The sensitivity to free alkalinity or acidity obtained with the cresol red-phenolphthalein indicator system is shown in Fig. 2. These results were obtained with a Cary 15 spectrophotometer and show that peak absorption occurs at approximately 577 mμ. Of the colorimeter filters available at the time this work was done, the one at 500 mμ was closest to this peak, and this proved to be satisfactory. This figure shows three typical curves. The lower represents 0.5% free fatty acid; the middle one, a neutral soap; and the upper one, a soap containing 0.04% free NaOH. It is obvious that, if the wavelength of the peaks had been used, it would be necessary to reduce the recorder response in some way to stay on scale for higher percentages.

TABLE I

Optical Density Related to Free Acid or Free Alkali

% Acid, as oleic	% NaOH	Optical density			
		White	Gold	Pink	Aqua
0.5		0.220	0.212	0.213	0.193
0.25		0.300	0.285	0.290	0.260
0	0	0.399	0.393	0.390	0.348
	0.02	0.494	0.490	0.484	0.433
	0.04	0.595	0.596	0.583	0.523
	0.06	0.689	0.684	0.680	0.593
	0.10	0.896	0.886	0.872	0.785

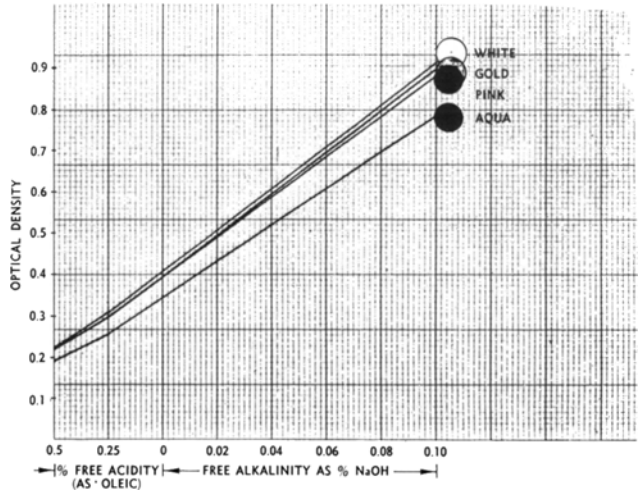

FIG. 3. Optical density related to free alkalinity or acidity content.

The procedure employed to calibrate the results was as follows: bar soaps of four colors (white, pink, aqua, and gold) were obtained and their alkalinity was determined by the AOCS Official Method. Then 5% solutions of these soaps were prepared in 50% alcohol. In preparing these solutions, sufficient standard acid or alkali was included to give solutions for each color containing 0.25 and 0.5% free acidity (calculated as oleic acid) or 0, 0.02, 0.04, 0.06, and 0.10% free NaOH. The solutions were filtered if insoluble matter was evident. These solutions were then put through the AutoAnalyzer to obtain the corresponding optical densities.

Five replicates were run for each test variable, and averages of the results are shown in Table I and in Fig. 3. It is readily seen that three of the colored soaps gave results which were quite similar. The aqua soap gave slightly lower optical densities because of a dye interference. However, the resulting curve was quite uniform. The optical densities are found to increase uniformly with the alkalinity content of the sample. In the range of optical densities, the precision obtained was ±2% in optical density units at the 95% confidence level. Precision was not found to vary with the color of the bar.

By taking the optical density of the solution for neutrality as the reference solution for each color of soap and by dividing the optical densities of the solutions of corresponding colors by these, the relationship shown in Table II was found.

It is evident that a definite pattern was established, and the method of calculation as given in the procedure was derived from this.

In considering results from unknowns, the attainable over-all accuracy of the method is ±0.0025% for free alkalinity and ±0.05% for free acidity, as oleic acid. The reference solution of white, pink, or gold could be used for all three colors with very slight

TABLE II

Optical Density of Various Solutions Divided by O.D. of Reference Solutions

% Acid (oleic)	% NaOH	White	Gold	Pink	Aqua
0.50		0.55	0.54	0.55	0.55
0.25		0.75	0.73	0.74	0.75
0	0	1	1	1	1
	0.02	1.24	1.25	1.24	1.24
	0.04	1.49	1.50	1.49	1.49
	0.06	1.73	1.74	1.72	1.70
	0.10	2.25	2.25	2.24	2.26

loss in accuracy. However, if the aqua reference solution were to be used for determinations on the other three colors, the results would be 0.01% high, or, if one of the other colors were used as reference solution for the aqua solutions, the results would be 0.01% low at the 0.04% level.

In conclusion, application of this method for quality and process control, although promising from the point of view of speed and accuracy, is now limited by the lack of a readily available sampling device. An automatic sampling device will allow fuller exploration of this promising approach.

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