The Automated Determination of Alkyl Aryl Sulfonates in Spray-Dried Detergents by Ultraviolet Absorption

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Abstract

An automated procedure has been developed for the determination of alkyl aryl sulfonates in spray-dried detergents. It is based upon the ultraviolet absorbance of alkyl aryl sulfonates at 224 mμ. A Technicon Solid Preparative Sampler is employed to dissolve the sample, dilute it to a fixed volume and remove an aliquot for analysis. The sample aliquots are continuously fed by a Technicon Proportioning Pump to a flow cell in a recording spectrophotometer. All operations, excluding sample weighing, are automatic and analyses can be carried out continuously at the rate of 10 samples per hour. The method has been found to have a coefficient of variation of 3.5%.

Introduction

Much of the powdered detergent currently available on the market is based upon the use of alkyl aryl sulfonates as the major surfactant. Many of these products are produced continuously, at high volume in spray towers and close analytical control is important in keeping the products within specifications. Manual analytical procedures for controlling large volume processes are obviously lacking in speed to be of great value in continuous control. It was to supply a need in this area that the automated procedure described in this paper was developed.

The determination of alkyl aryl sulfonates by ultraviolet absorption has been previously reported (1) and is an established ASTM and AOCS procedure (2,3). It is based upon the strong absorbance of alkyl aryl sulfonates in aqueous solution. An ultraviolet spectrophotometer equipped with a flow cell is used for multiple analysis, but the method is not automated in that sample weighing and dilutions must be performed for each determination. This paper is concerned with the automation of this basic technique using a Technicon SOLIDprep sampler and proportioning pump in conjunction with a recording spectrophotometer equipped with a flow cell.

Experimental Procedures

Principle

This method is based on the strong absorbance of alkyl aryl sulfonate in ultraviolet light. After a representative sample is manually weighed out, it is automatically dissolved in water and a sample aliquot removed and analyzed. For analysis, the sample aliquot is pumped through a spectrophotometric flow cell and the transmittance at 224 mμ is continuously measured and recorded. The active ingredient (alkyl aryl sulfonate) level is determined by comparison with a standard curve.

Apparatus used were Technicon SOLIDprep sampler, Technicon proportioning pump, recording spectrophotometer equipped to operate in the ultraviolet, quartz flow cell, 0.3 mm path length, powerstat variable transformer, type 3PN, 116. Reagents used were alcohol, specially denatured formula 3A, and water.

Sample Analysis

Assemble the modules as shown in Figure 1. Make all adjustments in accordance with instructions described in the operating manuals. Allow the entire system to equilibrate as determined by the flatness of the recorder baseline obtained using empty sample

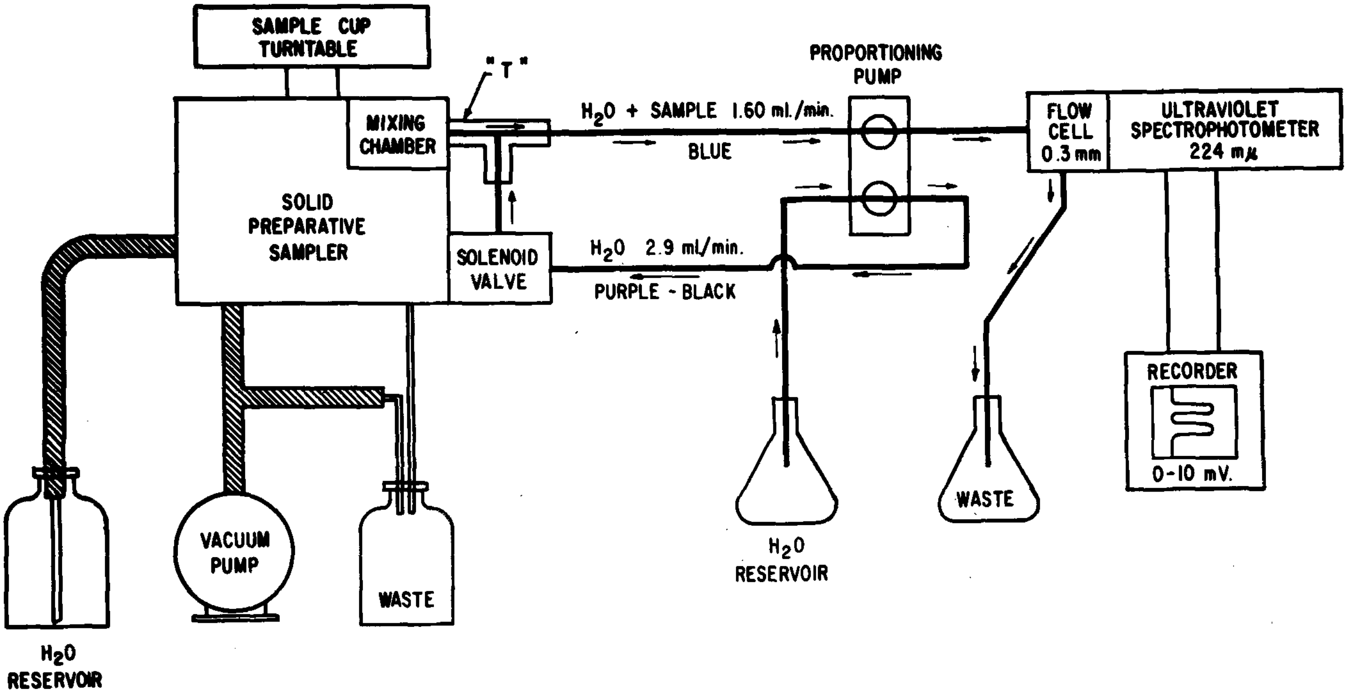

FIG. 1. Flow diagram of method.

cups on the SOLIDprep sampler. Rinse the sample cups with water and alcohol and permit to dry prior to instrumental adjustments. Accurately weigh (to the nearest 0.1 mg) representative samples containing between 0.18 to 0.23 g of alkyl aryl sulfonate into the sample cups. Place the sample cups on the SOLIDprep turntable leaving an empty cup between samples. The spacer cups will ensure through purging of the system between samples and will allow a return of the recorder trace to baseline between peaks. After the series of samples has been completed, record the peak heights obtained in centimeters from the baseline. The weight of alkyl aryl sulfonate corresponding to each peak height is obtained by reference to a standard curve. The level of active ingredient is then calculated as follows:

$$\frac{\text{Grams of active ingredient (from curve)}}{\text{Weight of sample}} \times 100 = \text{Per cent alkyl aryl sulfonate}$$

Standardization

Isolate a sample of the product to be used as a standard. Determine the alkyl aryl sulfonate level of this sample by the p-Toluidine method (6) or any other accepted procedure. Accurately weigh (to the nearest 0.1 mg) the correct weight of standard into the Technicon SOLIDprep sample cups equivalent to the following amounts of active ingredients: 0.10, 0.15, 0.175, 0.20, 0.225, 0.25 and 0.275 g. Analyze the standards by the automated method previously described. Draw a standard curve of peak height from the recorder (in centimeters) versus the grams of active ingredient.

Instrument Variables

Solid Preparative Sampler

In the earlier phases of this work a Technicon Sampler 1 was used to sample aqueous solutions of the detergent mixture. This had the disadvantages of extra preparation steps and the introduction of air bubbles into the system, making the recording of peaks somewhat irregular and difficult to measure. The work presented in this report was carried out using the SOLIDprep sampler (4) with the modifications given in the following paragraphs.

Since the normal operating speed of the stirrer during mixing is too fast and results in excessive foaming, a Powerstat is used to lower the operating speed of the stirrer during mixing. The speed of the disintegrator motor in the sampling phase is set at a slow mixing speed to keep the sample homogeneous during sampling. It is also helpful to pour 200 ml of 3A alcohol into the large vacuum waste bottle to reduce the amount of foaming caused by the sample discharge.

Although the instruction manual for the SOLIDprep sampler suggests an aspiration of the sample as it is being removed from the homogenizer, this is not necessary and also quite undesirable since the sample is passed immediately through the spectrophotometric flow cell. The sampling tube is connected directly to the outlet on the homogenizer and the wash water is introduced where the air inlet tube is normally fitted. These arrangements determine the requirements of the proportioning pump, discussed in the next section.

The Diluent Delivery dial is set to deliver 200 ml of water on each cycle.

TABLE I

Comparison of Results Obtained Using the p-Toluidine and the Automated Method

Sample	Per cent active ingredient (LAS)		
	p-Toluidine method	Automated method	Difference
1	18.74	20.05	1.3100
2	19.20	18.50	−0.7000
3	20.19	19.41	−0.7800
4	19.39	19.37	−0.0200
5	19.41	19.78	0.3700
6	20.47	20.88	0.4100
7	18.74	20.52	1.7800
8	19.20	19.53	0.3300
9	20.19	20.52	0.3300
10	19.39	18.50	−0.8900
11	19.41	20.12	0.7100
12	20.47	19.29	−1.1800

Mean of differences = 0.1391
Variance = 0.8941
Standard deviation = 0.945
t calculated[a] = 0.3571
t .05 (11 D.F.) = 2.201

[a] Since t calculated is less than t from the Tables, there is no significant difference between the two methods at the 95% confidence level.

Proportioning Pump (5)

Two pumping tubes are used on the proportioning pump. One tube pumps water at the rate of 2.9 ml/min into the SOLIDprep sampler to supply wash water at the outlet on the homogenizer. A second tube is used to pump the wash water and the sample aliquots from the homogenizer through the spectrophotometric flow cell at the rate of 1.60 ml/min.

Recording UV Spectrophotometer

The cell compartment is fitted with a 0.3 mm flow cell and carefully sealed to prevent any stray light from entering. The wavelength selector is set at 224 mμ and remains in this position during all analyses.

Results and Discussion

A series of samples of sprayed detergent was analyzed following the described procedure. All samples were of the same formulation and a standard curve was prepared as previously described. The p-Toluidine method (6) was chosen for the standardization. Results of the analysis by the automated procedure versus the p-Toluidine method on two random selections of samples from a spray tower run are shown in Table I. Statistical analysis has shown that there is no significant difference in results obtained by the automated method and the standard p-Toluidine method.

The precision of the automated method was checked by replicate analysis of a single sample of a spray-dried detergent. The data and results obtained in this study are shown in Table II. Precision analysis of the data yielded a coefficient of variation of 3.48 which indicates that the method is acceptable for routine analysis.

TABLE II

Precision of the Method

Active Ingredient as Determined by the Automated Method		
20.60	19.92	20.28
19.51	19.77	19.31
19.42	19.95	20.18
19.00	20.63	20.31
19.02	19.22	20.92
19.83	19.24	19.93
19.09	19.88	18.98
21.34	19.33	18.57

Statistical analysis: X = 19.76
n = 24
Standard deviation = 0.688
Coefficient of variation = 3.48

Further investigation showed the method to be applicable to the determination of alkyl aryl sulfonate in several products formulated with mixed active ingredient systems. Products containing ultraviolet absorbing materials such as sodium toluene or xylene sulfonates cannot be analyzed by the method because of their positive interference with alkyl aryl sulfonates. Although methods are available for removing interferences of this type (7), their use prior to analysis would increase analytical time to a point where the method would not be attractive for control purposes.

The original method (1) employed the use of absorptivity values in calculating the alkyl aryl sulfonate. This approach was found to be impractical in the current application, and calibration by a standard wet procedure was adapted. In some cases, the two-phase titration method using dyestuffs (8) may be found preferable to the p-Toluidine procedure. We have found that once the units are operating in a stable manner, an occasional spot check of a standard is all that is required to assure accurate results.

It is expected that it should be possible to eliminate the need for a standard curve by fixing sample weights and including a pre-analyzed sample of the same weight at desired intervals. This would eliminate calculations and allow simple visual checks of peak heights to determine compliance to specifications. If the density of the product is fairly uniform, it also appears possible to eliminate weighing completely by using a standard scoop to transfer samples to the cup.

The analytical system described appears to have other applications, some of which include: analysis of other absorbing species, analysis of effluents from chromatographic columns and studies of reaction kinetics. The technique also appears feasible for multiple analysis of the sample stream after emergence from the flow cell.

REFERENCES

1. Kelley, R. M., E. W. Blank, W. E. Thompson and R. Fine, ASTM Bulletin No. 237, p. 70–73, April 1959.
2. American Society for Testing Materials, Designation D 1768–62.
3. AOCS Tentative Method Dd 3–60.
4. Technicon, AutoAnalyzer Manual No. Sol-1.
5. Technicon, General Operating Instruction Manual, Section PP, p. 3–7.
6. Marron, T. U., and J. Schifferli, Ind. Eng. Chem., Annl. Ed. *18*, 49 (1946).
7. House, R., and J. L. Darragh, Anal. Chem. *26*, 1492 (1954).
8. American Society for Testing Materials, Designation D 1681–62.

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