different conditions. In Table I are shown the results of this series of tests. Analysis of variances, isolating possible sources of variations, and the application of the F-ratio test for homogeneity of variances are shown in Table II.

The following facts emerge from examination of these data. In the comparison of two different lots of soil cloth involving some 54 degrees of freedom, an F-ratio of 1.56 was indicated against the critical value of 1.57. This is a borderline situation. It is doubtful that different lots of soil cloth will produce different levels of precision of this method, based on these data.

Greater reproducibility occurs at 0.2% of detergent concentration in water of 50 p.p.m. total hardness than in harder waters. Since the ratio of the mean squares obtained at 135 p.p.m. and at 300 p.p.m. water hardness failed to exceed the critical value of F for the number of degrees of freedom involved, these mean squares are different estimates of the same

TABLE II
Analysis of Variance of Soil Removal at 0.2% of Detergent Concentration

Variable	Mean square	Degrees of freedom	F-ratio		Critical value of F
1. Soil cloth					
Lot 1	0.6956	54	F 2-1	= 1.56	1.57
Lot 2	1.0884	54			
2. Total hardness					
50 p.p.m.	0.5422	36	F 300-50	= 2.10	
135 p.p.m.	0.9944	36	F 135-50	= 1.83	1.75
300 p.p.m.	1.1394	36	F 300-135	= 1.15	
3. Detergent sample					
T_1	0.8192	18	F 1-2	= 1.11	
T_2	0.7371	18	F 3-1	= 1.51	2.29
T_3	1.2374	18	F 3-2	= 1.68	
C_1	1.0446	18	F1-2	= 1.69	
C_2	0.6168	18	F 1-3	= 1.16	2.29
C_3	0.8970	18	F 3-2	= 1.45	
4. Detergent type					
T	0.9312	54	F T-C	= 1.09	1.57
C	0.8528	54			

variability. Thus the data from these hardnesses can be pooled for a better estimate of the hard water variance.

Different lots of the same type of detergent give the same reproducibility, and the same precision can be obtained from different types of anionic detergents.

These data indicate that the method of reproducibility at a concentration of 0.2% in soft (50 p.p.m.) water is as follows: standard deviation equals 0.74% soil removal; precision equals 1.5% soil removal at a 95% confidence level. The data for hard water (135 or 300 p.p.m.) is as follows: standard deviation equals 1.03% soil removal; precision equals ± 2.06% soil removal at a 95% confidence level.

In a subsequent paper the precision of the method outlined herein will be presented at detergent concentrations other than at 0.2%.

Acknowledgment

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Statistical Approach to Detergency Evaluation. Correlation of Performance Data with Gas Chromatographic Patterns of Alkylbenzenes[1]

ERIC JUNGERMANN, G. A. DAVIS, E. C. BECK and W. M. LINFIELD, Soap Research and Development Department, Armour and Company, Chicago, Illinois

The precision of a standardized detergency test based on the use of a Tergotometer and U.S. Test Cloth was found at a concentration of 0.4 and 0.5%. At these concentrations, the standard deviation was 0.56% soil removal units, and precision at a 95% confidence limit was ± 1.12% soil removal units.

The detergency of some built spray-dried detergents was examined by this method and found to differ significantly, though chemical compositions were identical. Gas chromatographic analysis of the alkylbenzenes obtained by desulfonation of the alkylbenzene sulfonates indicated small structural variations which correlated with the observed variations in the detergency.

I N A PREVIOUS PAPER (3) a standardized procedure for determining the detergency of built detergent powders was described utilizing the Tergotometer and U.S. Test Cloth. It was found that when this test was run at a concentration level of 0.2% the precision was dependent on the hardness of the water being used. With soft water (50 ppm) the precision at a 95% confidence limit equalled ± 1.5% soil removal units; on the other hand at the 135 ppm and 300 ppm water hardness level the precision was ± 2.6% soil removal units. This indicates that for evaluating the relative cleaning ability of detergents, the 0.2% concentration level might lead to misleading results. This point is illustrated in Fig. 1, which shows typical soil removal vs. concentration curves. At the 0.2% concentration, the slope of the curve is still quite steep, and errors are readily magnified.

The purpose of this investigation was to determine whether the precision of our method could be improved by running the test at higher concentrations

which correspond to the more horizontal portions of the detergency curve. Detergency was determined at concentrations of 0.3, 0.4, and 0.5% at two water hardnesses and the results were evaluated by standard statistical methods.

Experimental

Detergency Evaluation. The general method described in a previous article was used in evaluating detergency except that the concentrations of detergent used were 0.3, 0.4, and 0.5% (3).

Desulfonation. The spray-dried detergents were desulfonated, using minor modifications of the procedure by Knight *et al.* (2). A 50 g. sample was used. The refluxing pot was equipped with a condenser and bottom-return receiver in order to retain the free alkylate as it was distilled. The recovered alkylate was washed with water until free of acid, and dried over calcium sulfate.

Chromatography of Alkylate. The free alkylate was chromatographed under the following conditions:

Column temperature............................200°C.
Column packing.................................20% Apiezon M
Column length.....................................4 ft.
Carrier gas..Helium
Carrier flow rate.................................100 ml./min.
Preheater temperature.......................250°C.
Detector..Gow-Mac TEII

Chromatograms so prepared are characteristic of the type and quality of original alkylate used. An instrument designed in our laboratory and described in a previous paper entitled "Identification of Soap Stocks by Gas Chromatographic Techniques" was used (1).

Measurement of Pattern Obtained. The pattern obtained was compared with a reference pattern, peak by peak, by measuring the absolute peak height in mm. from the apex of the peak to a horizontal line drawn from the base of each peak. For peaks numbered 1-3, the base line was drawn from the base of the left side to the base of the right side of each peak; for peaks numbered 4-9, the base line was drawn horizontally from the base of the right side. The ratio of the height of peak one of the sample to the height of peak one of the reference forms the basis of equating the chromatograms to each other. A typical curve is shown in Fig. 2.
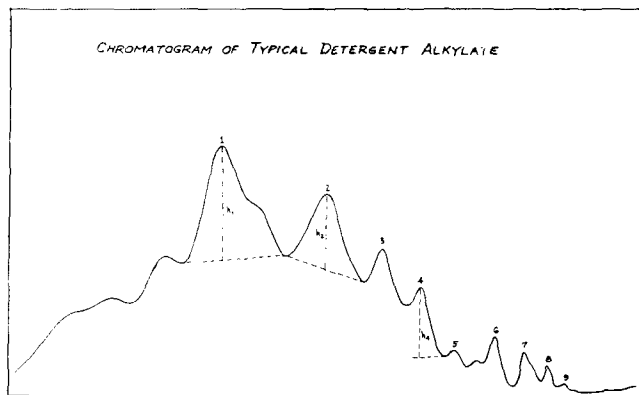

FIG. 1. Three typical detergent curves.

FIG. 2. Chromatogram of alkylbenzene.

Results and Discussion

In this series of detergency tests, a single lot of soil cloth was used to evaluate, in quadruplicate, four batches of a typical spray-dried anionic heavy-duty detergent in soft (50 ppm) and hard (300 ppm) water at concentrations of 0.3, 0.4, and 0.5%. The detergency results obtained are shown in Table I and the variance analysis and F-ratio tests are shown in Table II. The statistical methods used are those discussed in a previous paper (3). The data in the Analysis of Variance, Table II, show that none of the variance ratios exceeds its respective critical value of F at the 0.05 probability level. There is no evidence, therefore, that a variance component exists either at concentration levels of 0.3, 0.4, and 0.5%, or by water hardness variations. This differs from our previously reported results at the 0.2% concentration, where water hardness was found to be a component variance (3). Hence, there is no statistical necessity for using more than one of these hardnesses or concentrations for each test. Since all of the variances of precision arise from inherent experimental error only, they can be pooled for a better estimate of the method's precision. From 72 degrees of freedom contained in the set of data for computing replicate reproducibility the following estimates of single test precision are obtained:

Variance = 0.3159.
Standard Deviation = 0.56% soil removal units.
95% Confidence Limits = ± 1.12% soil removal units.

Since the ± 1.12% gives the area within which the true value lies it follows that if single evaluation results on two different detergents are more than 2.24% units apart, the probability is less than 5% that the samples come from the same statistical universe or, in other words, they are significantly different in a statistical sense. If, instead of a single determination, the experiments are carried out in quadruplicate, the precision is increased to ± 0.56 units.

Application of the Statistical Method

Having thus determined the limitations of our particular detergency test, a practical example of ranking the washing efficiency of a set of four detergent powders was obtained by examining the average soil removal values at 0.4% and 0.5% concentrations. The values were compared with those obtained from a so-called standard sample of identical composition. The mean results from quadruplicate tests are shown in Table III.
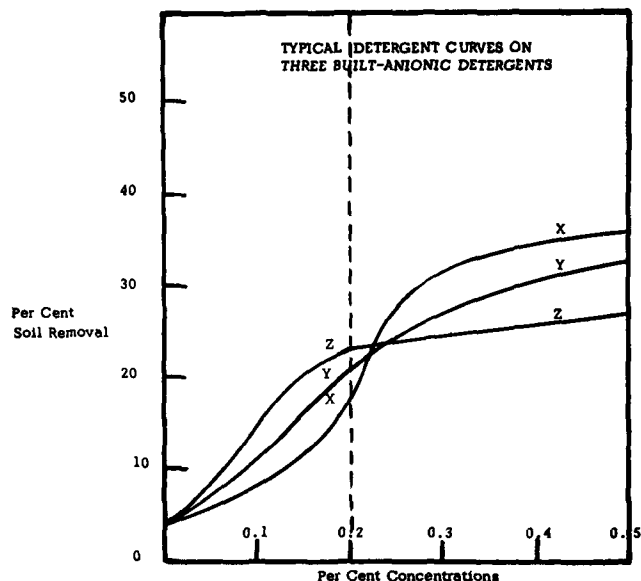
TABLE I
Percentage Soil Removal at Three Detergent Concentrations

Sample	#1			#2			#3			#4		
Concentration,%	0.3	0.4	0.5	0.3	0.4	0.5	0.3	0.4	0.5	0.3	0.4	0.5
50 ppm water hardness Run												
1	26.4	29.2	30.6	26.9	26.4	28.5	25.5	26.9	30.3	26.7	28.0	31.2
2	28.4	29.3	32.0	25.6	27.6	29.4	24.6	27.7	29.5	26.8	28.9	31.6
3	26.9	29.4	30.8	25.9	27.5	29.0	25.8	28.0	29.0	26.5	29.1	30.6
4	27.2	29.8	31.2	26.3	27.4	29.2	26.3	26.0	30.1	26.3	29.3	30.9
Avg	27.2	29.4	31.2	26.2	27.2	29.0	25.6	27.2	29.7	26.6	28.8	31.1
300 ppm water hardness Run												
1	27.6	29.9	30.3	25.3	27.4	28.9	25.2	27.7	29.2	26.3	29.1	31.6
2	27.0	29.6	31.3	24.9	28.1	28.0	25.9	28.0	28.6	26.1	29.2	30.5
3	26.6	29.2	31.7	24.9	27.6	28.7	25.4	27.0	28.7	26.5	29.2	30.1
4	27.0	30.2	32.5	25.8	27.5	29.0	24.7	26.7	28.7	27.3	28.5	29.7
Avg	27.0	29.7	31.4	25.2	27.6	28.6	25.3	27.4	28.8	26.6	29.0	30.5

Examination of the data presented in Table III shows that two of the samples, A and D, have a detergency equal to the standard, while the other two are significantly less efficient. Thorough checks of the relative composition of these four mixtures as well as the sources of the raw materials by standard analytical techniques indicated that no compositional variations in the formulation existed.

TABLE II
Analysis of Variance:
Three Detergent Concentrations and Two Water Hardnesses

Variable	Mean square	Degrees of freedom	F—ratio	Critical value of F
1) Concentration				
a) at 50 ppm:				
0.3%	0.3994	12	F .3–.4 = 1.06	2.69
0.4%	0.3777	12	F .3–.5 = 1.50	
0.5%	0.2660	12	F .4–.5 = 1.62	
b) at 300 ppm:				
0.3%	0.2188	12	F .3–.4 = 2.36	2.69
0.4%	0.1856	12	F .5–.3 = 2.04	
0.5%	0.4480	12	F .5–.4 = 2.44	
2) Hardness				
a) 0.3%:				
50 ppm	0.3994	12	F 50–300 = 1.82	2.69
300 ppm	0.2188	12		
b) 0.4%:				
50 ppm	0.3777	12	F 50–300 = 2.04	2.69
300 ppm	0.1856	12		
c) 0.5%:				
50 ppm	0.2660	12	F 300–50 = 1.68	2.69
300 ppm	0.4480	12		
3) Hardness at all concentrations:				
50 ppm	0.3477	36	F 50–300 = 1.22	1.75
300 ppm	0.2842	36		

Gas Chromatography of the Dodecylbenzene

Since chemical analyses indicated no variations in the formulations, the composition of the alkylaryl sulfonates which were part of the detergent system were examined. The analytical technique which was employed was based on the following combination of procedures: the alkylaryl sulfonate is first desulfonated with concentrated phosphoric acid, and the desulfonated oil gas chromatographed. The curve obtained under these conditions is shown in Fig. 2. It is typical of the source and type of alkylaryl sulfonate used, and careful comparison of the height of each peak

relative to a known reference curve allows detection of minor raw material variations. The measurements for these comparisons were done in a standardized way and are reproducible. The results obtained on the four detergent samples and the standard are shown in Table IV. On examining the peak heights thus obtained, two trends were at once apparent: first, when comparing the peak height of the No. 1 and 2 peaks, it was noted that in the case of samples A and D, as well as in the case of the standard, this ratio was higher than unity. In the case of the other two samples, B and C, which had inferior detergency, this ratio was approximately equal to unity. Secondly, when comparing the height of the No. 4 peak, it was found to be considerably higher in samples B and C than in samples A and D and the standard. This work was extended to a large number of samples and it was found that this relation held throughout whenever this particular grade of alkylbenzene sulfonate was used.

One alternate approach to evaluating these gas chromatograms was based on summing algebraically all the relative peak heights. Two methods of summation were used: the first used peak No. 1 as a reference peak for all calculations, while the second method used the total sum of all peaks as a reference for summation. In the first method, changes in parameters which would affect the chromatograms as a whole were cancelled by equating to the number one peak. This assumed, of course, that the number one peak is changeless, which is usually, but not always, true. The second method was to count each peak as a percentage of the sample total. This is a function of the composition of the sample only and is independent of chromatographic variables.

It was found that whenever the total deviation had a high plus value (>2.5) the sample had inferior detergency. On the other hand, deviations below 2.5 always correspond to samples with the higher detergency. It was realized that these methods of summa-

TABLE III
Evaluation of Four Built Detergents at 50 ppm and 300 ppm Water Hardness

Sample	A		B		C		D		Standard	
Concentration, %	0.4	0.5	0.4	0.5	0.4	0.5	0.4	0.5	0.4	0.5
Soil removal % (mean of 4)										
50 ppm	29.4	31.2	27.2	29.0	27.2	29.7	28.8	31.1	29.6	32.0
300 ppm	29.7	31.4	27.6	28.6	27.4	28.8	29.0	30.5	29.2	31.4
Conclusion, detergency relative to standard	Same		Inferior		Inferior		Same			

Standard deviation = σ = 0.56%.

Standard error of mean (4) = $\sigma/\sqrt{n}$ = 0.56/2 = 0.28%.

95% Confidence limits of mean = ± 0.56%.

TABLE IV
Chromatograms of Alkylbenzenes

Sample	A	B	C	D	Reference
Detergency	Good	Bad	Bad	Good	Good
Peak #					
1	21.8	20.9	19.3	24.2	25.6
2	18.8	21.0	19.7	21.5	17.4
3	11.6	13.1	11.3	14.1	9.8
4	14.1	19.1	19.4	15.7	16.2
5	4.1	5.0	5.3	3.3	3.9
6	11.7	11.5	12.5	9.6	11.3
7	9.2	6.1	7.4	6.6	6.0
8	5.2	2.1	3.3	2.9	5.6
9	3.5	1.2	1.8	2.0	4.2
Σ σ Method I	+1.13	+1.68	+3.63	−1.75	0
Σ σ Method II	+2.08	+2.99	+4.48	−0.83	0

tion contain some dangers, since big positive deviations can be cancelled out by big negative deviations; therefore, it was preferable to compare individual

peaks, particularly the ratio of the first two peaks as well as the No. 4 peak, as described earlier.

It was concluded from these correlations that some quite minor variations in the nature of the alkylbenzene sulfonate, not detectable by standard analytical techniques, could greatly affect detergency. This gas chromatographic technique of checking the alkylbenzene sulfonates can be used effectively to assure both the quality and the standard of a particular formulation, as well as product uniformity.

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Identification of Soapstocks by Gas Chromatographic Techniques [1]

E. C. BECK, E. JUNGERMANN, and W. M. LINFIELD, Soap Research and Development Department, Armour and Company, Chicago, Illinois

The stock of a given soap may be estimated when the ratios of the fatty acids present are known. A new gas chromatographic procedure utilizing a novel automatic attenuator is presented. The samples are prepared by refluxing the soap with a methanolic solution of boron trifluoride and separating the esters so formed by standard gas-liquid chromatographic procedures. Soapstock compositions are determined by comparison with reference curves.

THE STOCK of a given soap may be determined if the fatty acid composition is known. This is accomplished in many laboratories by performing a number of average physical and chemical measurements such as titer, saponification value, and iodine number (1). These measurements fail to give a complete picture when the soapstock has been partially hydrogenated, when different sources of tallow are employed, and when blends containing other than tallow and coconut are utilized. In addition, the above mentioned measurements are time consuming. Primarily, tallow is a triglyceride of stearic, oleic, and palmitic acids; coco is a triglyceride of lauric and myristic acids.

Gas-liquid chromatography of fatty methyl esters have been widely reported in the literature (2, 4, 5). More recently chromatographic separation of fatty acids has been accomplished without preparation of the corresponding methyl esters (8). The quantitative relationship of individual peak areas and composition of fatty methyl ester chromatograms is also well documented (3, 6, 7). Utilizing an instrument equipped with a novel automatic attenuator, the techniques of gas-liquid chromatography have been applied to the study of soapstocks.

Experimental

Reagents. (1) Boron trifluoride in methanol, prepared by dissolving 120 g. of boron trifluoride in 1 l. of methanol. The solution requires refrigeration. (2) One g. of sodium metal dissolved in 10 ml. of

methanol. This solution is unstable and needs to be prepared daily.

Instrument. Laboratory-built chromatograph, utilizing a Leeds and Northrup recorder, with Gow-Mac thermal conductivity cell.

Sample Preparation. Soap samples to be chromatographed are first warmed with 6% sulfuric acid. The fatty acids so liberated are then heated with an equal volume of warm boron trifluoride in methanol according to the method of Metcalfe, et al. (9). The esters which form are insoluble in water and float to the top. Washing is unnecessary and separation may be accomplished with the aid of a separatory funnel. If analyzing the soap feed stock instead of the soap, that is triglycerides, esterification is accomplished by refluxing with freshly prepared sodium methoxide.

Chromatographic Conditions. The fatty methyl esters are chromatographed under the following conditions:

Column temperature...................200°C.
Column packing...........................Craig polysuccinate
Column length..............................5 feet
Column diameter..........................¼ in. O.D.
Carrier gas....................................Helium
Carrier gas flow rate...................100 ml./min.
Preheater temperature...............250°C.
Detector..Gow-Mac Model TE II
Recorder..Leeds and Northrup Speedomax G

Results and Discussion

The Instrument. To get a true insight into the composition of soapstocks, attention must be paid to both minor and major peaks. To accomplish this, the gas chromatographic instrument must couple sensitivity with attenuation so that all peaks, whether major or minor, are shown in proper relation on the same chart paper. For this purpose a decimal attenuator was constructed, the details of which are shown in Fig. 1.

The heart of the attenuator is the four-gang Uniselector switch, manufactured by the General Electric Co., of England. Gang one of the switch contains