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 results. 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 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

The authors wish to extend their thanks to R. M. Raschke, who performed much of the experimental work leading up to the standardization of method, and to G. A. Davis, who designed the statistical pattern and calculated and collated the findings.

REFERENCES

3. Harris, Jay C., ibid., 27, 564 (1950).
5. Harris, Jay C., ibid., 29, 110 (1952).

[Received May 26, 1961]

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


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 detergent.

In 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 equaled ± 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.

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.