Accuracy and Precision of the Analytical Results Obtained in Soap Analysis

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ALTHOUGH adequate analytical procedures, as typified by the "Official and Tentative Methods of Analysis of the American Oil Chemists' Society," (1, 2) are available to cope with the increasing complexity of composition of present day soaps and soap mixtures, there has been little discussion in the literature of the accuracy and reproducibility of the values obtained as a result of employing these methods.

The terms *accuracy* and *precision* are variously defined and employed, and for this reason they shall be defined at the outset. Accuracy is taken to express the correctness of an analytical result, and precision the reproducibility of an analytical result. A third term which is also commonly misused is *error* and this may be defined as the difference between the analytical result obtained and the true quantity of the constituent present in the sample.

Classification of Errors

Errors may be classified as determinate and indeterminate. Crumpler and Yoe (3) speak of determinate errors as those about which one can do something and indeterminate errors as those about which one can do nothing. This furnishes a rough working classification.

Determinate errors may be due to faulty instruments, reagents, mistakes in calculation, errors of omission, etc. (4). The remedy for most of the causes of determinate errors is evident. Indeterminate errors are also known as accidental errors. As their cause is unknown they cannot be counteracted by the application of corrections.

The subject matter of this paper is concerned mainly with indeterminate errors. It must be realized, however, that the results presented are also subject to undetected determinate errors. Every effort was made during the course of this investigation to reduce the magnitude of the determinate errors. The fact that only two results out of a total of several hundred had to be discarded augurs well for the reliability of the analytical work.

Conditions conducive to errors are continually arising in the course of analytical work and even the most skilled analyst occasionally falls a victim to them. If the analytical work is above reproach, any irregularity occurring during the course of an analysis should be examined with a view toward discovering, if possible, whether it represents abnormality of the sample rather than arbitrarily assuming it to be the result of an accident and blindly running check values in the hope that ultimately the analysis will right itself.

Limits of Error

The analysis of a soap never adds to exactly 100% except fortuitously, nor can an analysis be exactly reproduced on duplication. Experienced analysts can obtain repeat values within small limits of error. Naturally the limits of error vary with the proportion of each constituent present.

The limits allowed in this laboratory for the summation of a soap analysis are ordinarily 99.50 to 100.50%. Most of the errors in soap analysis, excluding physical losses, are additive. This includes errors due to the reagents carrying traces of the constituent sought, the hygroscopic nature of many ignited precipitates, over-titration of endpoints, co-precipitation, etc. However, these errors are over-balanced in their effect by a large negative error due to the volatilization of fatty acids during the operation of heating to constant weight. For this reason analytical summations usually total less than 100%. A total slightly in excess of 100% is probably theoretically more nearly correct analytically than a value under 100%.

Totals for 50 complete soap analyses of different samples of the same type of sprayed soap product were selected at random and the most probable value calculated. The summations ranged from a minimum of 99.43% to a maximum of 100.59%. The most probable value calculated to 100.00%.

Another unselected group of 18 summations on a flake soap product gave a most probable value of 100.01% with extreme individual summations ranging from a minimum of 99.52% to a maximum of 100.46%.

If an analytical summation lacks 100% by adding, for instance, to only 98% it is senseless to check values which ordinarily never approach 2.0%. Thus, one would not redetermine iron, unsaponified material, free caustic alkali, or any one of the several other determinations that ordinarily run quite low, of the order of magnitude of tenths of one per cent, yet one frequently discovers analysts laboriously repeating a whole analysis to discover the constituent which is in error without considering the magnitude of the error.

Precision of the Total Fatty Acid Plus Unsaponifiable Determination (5)

The precision of the total fatty acid plus unsaponifiable determination was established by having the total fatty acid plus unsaponifiable run on a soap sample 18 times by an experienced analyst. Values obtained varied from a low of 62.19% to a high of 63.28%. The mean (or most probable value) was 62.69%. The mean deviation, representing the amount by which an average single independent value differed from the most probable value was 0.16% and the average deviation of the mean was ± 0.039.

Explanation of Tables I to III

Table I summarizes the data obtained on a commercial sprayed soap analyzed by nine analysts, none of

TABLE I

Limits of Error on a Commercial Sprayed Soap Analyzed by Nine Analysts With Minimum Individual Experience in Soap Analysis of One Year.

Constituent	Most Probable Value * %	Extreme Values %	Mean Deviation %	Average Deviation of the Mean %
Moisture (Xylol Distillation)	7.17	7.00- 7.47	0.11	±0.036
Total Fatty Acids	59.45	59.05-60.05	0.22	±0.073
Total Fatty Acids + Unsaponifiable	60.09	59.68-60.60	0.19	±0.063
Free Fatty Acid	nil	nil	.....	.....
Unsaponified as Na_2O	0.02	0.01- 0.03	0.0050	±0.0018
Unsaponifiable	0.61	0.52- 0.67	0.039	±0.014
Anhydrous Soda Soap	64.73	64.36-65.00	0.22	±0.073
Glycerol	0.40	0.37- 0.47	0.023	±0.0077
Total Alkali as Na_2O	16.57	16.22-16.96	0.18	±0.060
Free Caustic as Na_2O	0.02	0.00- 0.04	0.011	±0.0037
Combined Alkali as Na_2O	7.45	6.95- 7.56	0.11	±0.037
Alcohol Insoluble	27.41	27.03-27.87	0.12	±0.041
Total Alkali of Filler as Na_2O	9.12	8.80- 9.40	0.17	±0.057
Sodium Carbonate	5.21	5.01- 5.53	0.11	±0.037
Silica (SiO_2)	10.53	10.21-10.86	0.14	±0.047
Na_2O Combined with SiO_2	2.35	2.09- 2.63	0.13	±0.043
Ratio Na_2O : SiO_2	1:3.38 to 1:5.13	.....	.....	.....
Na_2HPO_4	0.57	0.24- 0.88	0.15	±0.050
$Na_4P_2O_7$	7.47	7.28- 7.63	0.10	±0.033
NaCl	0.39	0.27- 0.51	0.053	±0.018
Na_2SO_4	0.22	0.15- 0.32	0.042	±0.014
Fatty Acid Constants				
Titer, °C	31.7°	31.2°-32.1°	0.21°	±0.070°
Iodine Value	42.1	40.6 -42.9	0.58	±0.19
Acid Value as KOH	22.54	22.14-22.74	0.14	±0.047
Saponification Value as KOH	22.61	22.31-22.75	0.14	±0.047
Lovibond Color: 1-Inch Cell	.....	70Y, 19R to 70Y, 25R	.....	.....

* Totaling the most probable values gives a summation for the soap analysis of 99.65%.

whom had less than one year of experience in the analysis of soap. A few of the analysts had over five years of experience. Considering the large number of analysts the spread between the extreme values is very small. Totaling the most probable values gives a summation for the soap analysis of 99.65%.

Table II is a repetition of the work done in preparation of Table I with the exception that it was carried out two years subsequent to the gathering of data for Table I. The significant difference is that the six analysts participating in the work had experience in soap analysis of one year or less. It will be apparent from a comparison of the data in the two tables that the accuracy and precision of the data in Table II are somewhat inferior. This clearly confirms the old precept that practice is essential to achieve perfection.

Table III indicates the precision and reproducibility of results of a single analyst with experience of about one year in the analysis of soap.

The Value of Accuracy and Precision Data

Most of the determinations were run according to the "Official and Tentative Methods of Analysis of the American Oil Chemists' Society" with the exception of several slight variations of procedure. The results are therefore of interest in demonstrating the accuracy and precision of values obtained by employing the Official Methods.

Frequently in checking against specifications an analytical result is obtained that is slightly higher (or lower) than the maximum (or minimum) permitted by the specification. In such an event the value of accuracy and precision data is evident. One

TABLE II

Limits of Error on a Commercial Sprayed Soap Analyzed by Six Analysts With Maximum Individual Experience in Soap Analysis of One Year.

Constituent	Most Probable Value* %	Extreme Values %	Mean Deviation %	Average Deviation of the Mean %
Moisture (Xylol Distillation)	13.12	12.82-13.33	0.20	±0.082
Total Fatty Acids	56.13	55.68-56.97	0.36	±0.15
Total Fatty Acids + Unsaponifiable	58.54	58.12-59.11	0.29	±0.12
Free Fatty Acid	nil	nil	.....	.....
Unsaponified as Na_2O	0.04	0.01- 0.10	0.023	±0.0093
Unsaponifiable	2.40	2.14- 2.80	0.15	±0.061
Anhydrous Soda Soap	60.75	60.34-61.61	0.23	±0.094
Glycerol	0.25	0.11- 0.39	0.090	±0.037
Total Alkali as Na_2O	16.26	15.98-16.47	0.15	±0.061
Free Caustic as Na_2O	0.008	0.00- 0.02	0.0065	±0.0027
Combined Alkali as Na_2O	6.51	6.40- 6.59	0.057	±0.023
Alcohol Insoluble	23.56	23.00-24.26	0.19	±0.078
Total Alkali of Filler as Na_2O	9.74	9.40-10.02	0.19	±0.078
Sodium Carbonate	12.94	12.29-14.11	0.74	±0.30
Silica (SiO_2)	6.80	6.35- 7.27	0.44	±0.18
Na_2O Combined with SiO_2	1.74	0.97- 2.31	0.45	±0.18
Ratio Na_2O : SiO_2	1:2.86 to 1:5.96	.....	.....	.....
Na_2HPO_4	0.39	0.28- 0.52	0.080	±0.033
$Na_4P_2O_7$	0.63	0.41- 0.81	0.11	±0.045
NaCl	0.57	0.53- 0.63	0.028	±0.011
Na_2SO_4	0.32	0.23- 0.40	0.050	±0.025**
Fatty Acid Constants				
Titer, °C	34.2°	33.8 -34.5°	0.32°	±0.13°
Iodine Value	63.5	61.9 -65.7	1.15	±0.47
Acid Value as KOH	20.17	19.89-20.51	0.17	±0.069
Saponification Value as KOH	20.37	20.07-20.60	0.13	±0.053
Lovibond Color: 1-Inch Cell	.....	70Y, 4.5R, to 70Y, 7R	.....	.....

* Totaling the most probable values gives a summation for the soap analysis of 99.91%.
** Two results omitted in tabulating data.

TABLE III

Precision of Results of an Individual. (H. M. Winegard)[1]

Constituent	Determination No.			Most Probable Value %*	Mean Deviation %
	1	2	3		
Moisture (Xylol Distillation)	14.08	14.28	14.35	14.24	0.10
Total Fatty Acids	55.75	55.84	56.13	55.91	0.15
Free Fatty Acid	nil	nil	nil	.....	.....
Unsaponified as Na_2O	0.01	0.01	0.02	0.01	.....
Unsaponifiable	2.18	2.21	2.29	2.23	0.043
Rosin Soda Soap	5.73	5.92	6.01	5.89	0.10
Anhydrous Soda Soap	60.39	60.49	60.81	60.56	0.16
Glycerol	0.13	0.17	0.21	0.17	0.027
Total Alkali as Na_2O	16.35	16.37	16.39	16.37	0.013
Free Caustic as Na_2O	nil	nil	nil	.....	.....
Combined Alkali as Na_2O	6.53	6.56	6.59	6.56	0.020
Alcohol Insoluble	23.20	23.20	23.39	23.26	0.083
Total Alkali of Filler as Na_2O	9.78	9.79	9.86	9.81	0.033
Sodium Carbonate	11.89	11.92	12.50	12.14	0.28
Silica (SiO_2)	7.04	7.13	7.15	7.11	0.043
Na_2O Combined with SiO_2	2.01	2.34	2.40	2.25	0.16
Ratio $Na_2O : SiO_2$	1:2.9	1:3.1	1:3.5	.....	.....
Na_2HPO_4	0.30	0.34	0.42	0.35	0.043
$Na_4P_2O_7$	0.66	0.69	0.71	0.69	0.017
NaCl	0.45	0.48	0.50	0.48	0.017
Fatty Acid Constants					
Titer, °C	34.1°	34.2°	34.6°	34.3°	0.20°
Iodine Value	56.7	57.7	58.4	57.6	0.60
Acid Value as KOH	20.41	20.41	20.44	20.42	0.013
Saponification Value as KOH	20.57	20.57	20.62	20.59	0.023
Lovibond Color: 1-Inch Cell	70Y	70Y	70Y	.....	.....
	3.5R	4.9R	5.3R	.....	.....

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* Totaling the most probable values gives a summation for the soap analysis of 100.22%.

is justified in stating the sample meets specifications if its apparent deviation from the specification is less than the demonstrated average deviation of the mean.

No results were discarded in summarizing the data with the sole exception of two values indicated in Table II. The analysts cooperating in the program were familiar with the object of the analysis but were not encouraged to compare results with one another until completion of the work. A number of analysts had to repeat several determinations because their analyses did not meet the criterion that the summation of the analysis fall between 99.50 and 100.50% for acceptance.

The data indicate that there is a significant increase in the degree of precision and reproducibility comparable with the increase in experience of the analyst, the degree of precision and reproducibility apparently rising to a maximum after about one year of experience. A good deal, of course, depends upon the aptitude of the analyst but the data do indicate that there is an initial period of varying duration, during which an inexperienced chemist is unable to attain the maximum accuracy and precision of the methods even though the results are still sufficiently accurate to be acceptable.

Comparison of the data in Tables I and II will reveal that the mean deviation for the determination of anhydrous soda soap apparently did not show improvement commensurate with the experience of the analysts. One other anomaly presents itself. The mean deviation for the sodium chloride value is almost twice as great for the more experienced analyst as for those with less experience. Possibly the old adage that familiarity breeds contempt is operative here. On the other hand, these irregularities might not have arisen if the individual analytical results had been weighed and evaluated before being incorporated in the tables.

The results given in Table I are probably more accurate than those generally encountered in industrial practice. On the other hand, they probably do not represent the very highest accuracy attainable but the latter would require the expenditure of an inordinate amount of time and normally would not be economically justifiable.

In closing, it should be emphasized that the usual textbook statements concerning the accuracy of various analytical procedures generally refer to the analysis of pure compounds. Such statements do not enable one to predict with any degree of confidence the accuracy of the same determination in the analysis of a material as complex as soap. It is only by repeated analysis of a soap and statistical study of the results that any indication can be had of their probable degree of accuracy and precision.

Acknowledgments

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