Deviation Frequency Distribution of Smalley Foundation Oil and Nitrogen Results

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THE writer is not a statistician and is not qualified to make a thorough statistical examination of data. However, a superficial tabulation and study of some of the 1945-46 Smalley Foundation Check Meal results were made. The accompanying histograms and the tentative conclusions offered may be of interest to the Check Meal collaborators. Possibly some one may carry the study to more positive conclusions.

The nitrogen results on the 1945-46 Check Meals 1 through 20 (1,500 results) were tabulated and grouped according to deviation magnitude from the Accepted Average in class intervals of ±.01% (see histogram). Oil results were listed likewise, except that samples 1 through 26 were used in order to obtain an equal total number of 1,500 oil results. Histograms are also shown for oil and nitrogen on each of the Check Meal reports 1 through 10.

The histograms of 1,500 oil and nitrogen results show a higher kurtosis, or degree of peakedness, for nitrogen, which was expected because of the greater accuracy of the nitrogen determination. The wide spread of results above the Accepted Average for oil, and below for nitrogen, or positive and negative skewness, respectively, was not anticipated. This reversal of skewness, however, applies only to results deviating rather widely from the Accepted Average. Those within a tolerance of ±.12% give approximately the same pattern, as shown in the tabulation below.

This trend of reverse skewness of oil and nitrogen results suggests certain conjectures. Wide deviations on oil will more often be high, due perhaps to such factors as incomplete evaporation, moisture in the extraction flask, or solvent with high evaporation residue. Wide nitrogen deviations are more often low. Such factors as under or over digestion, incomplete distillation, and still leakage produce low results.

The low kurtosis which appears in the single Check Meal histograms for oil, or dual and multiple peakedness may be due to deviations from uniform analytical practice among the collaborators. A questionnaire of several years back, which is not available here, may settle this point. Without the benefit of the data obtained at that time it is presumed that analysts may differ on two practices:

(1) Preëxtraction of filter paper or deduction of blank;

(2) Oven drying of extraction flasks.

Oven drying after evaporation for 30 minutes at 101° C., in this laboratory, gives results averaging .03% oil higher than complete drying on the steam bath. Whether this is due to oxidation or to the complete discharge of static electricity has not been determined. Complete uniformity in such analytical details as these might narrow the oil results' spread and increase the kurtosis. The Smalley Foundation Committee may find it possible to advise the collaborators on these and other details.

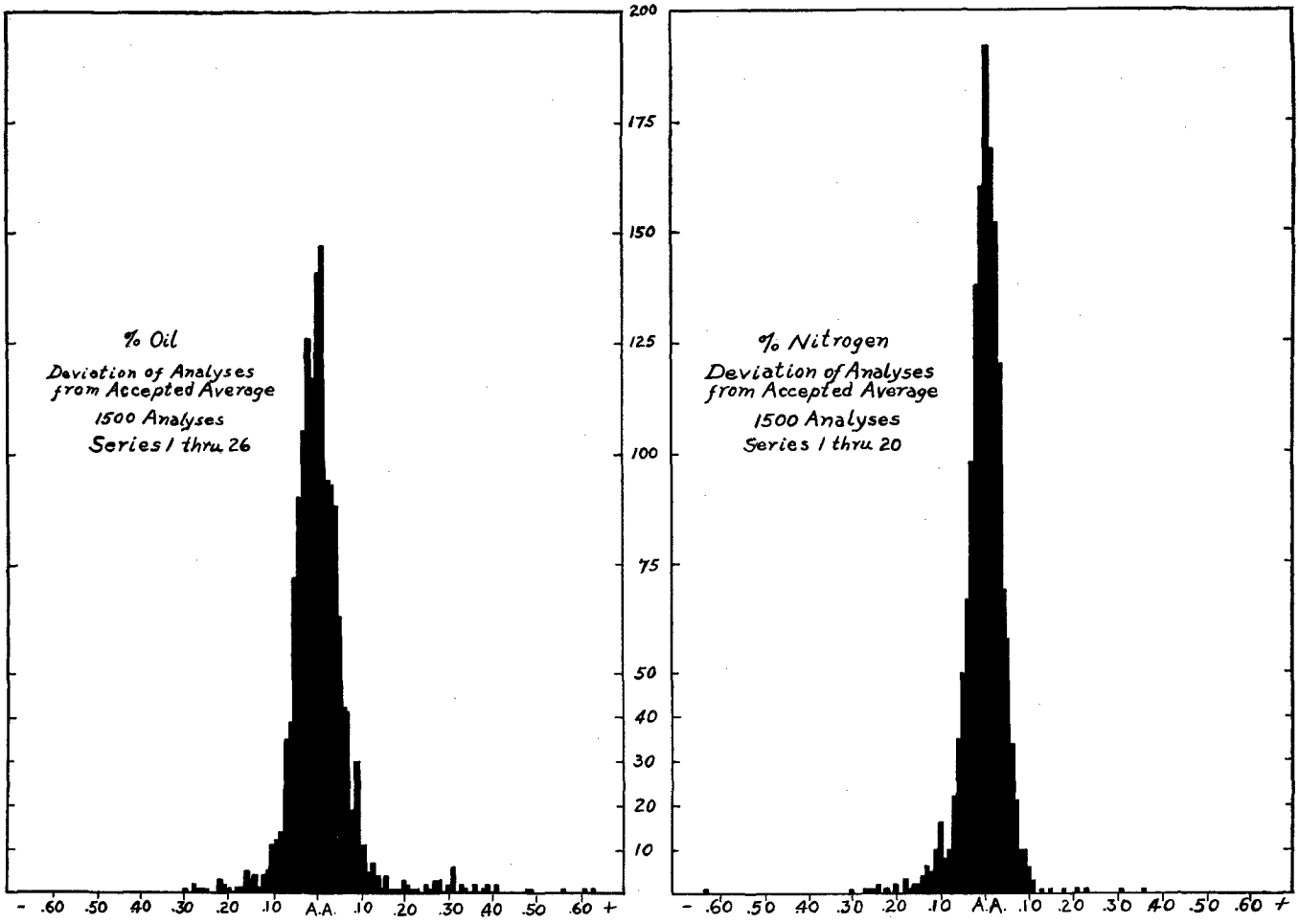
The Report of the Special Committee on Check Samples, Oil & Soap, March, 1946, gave the present method of calculating the Accepted Averages. It was recommended that the methods of calculating individual percentage standings of collaborating laboratories be reviewed critically "with the view to the adoption of more modern statistically accepted procedures in analysing comparative data."

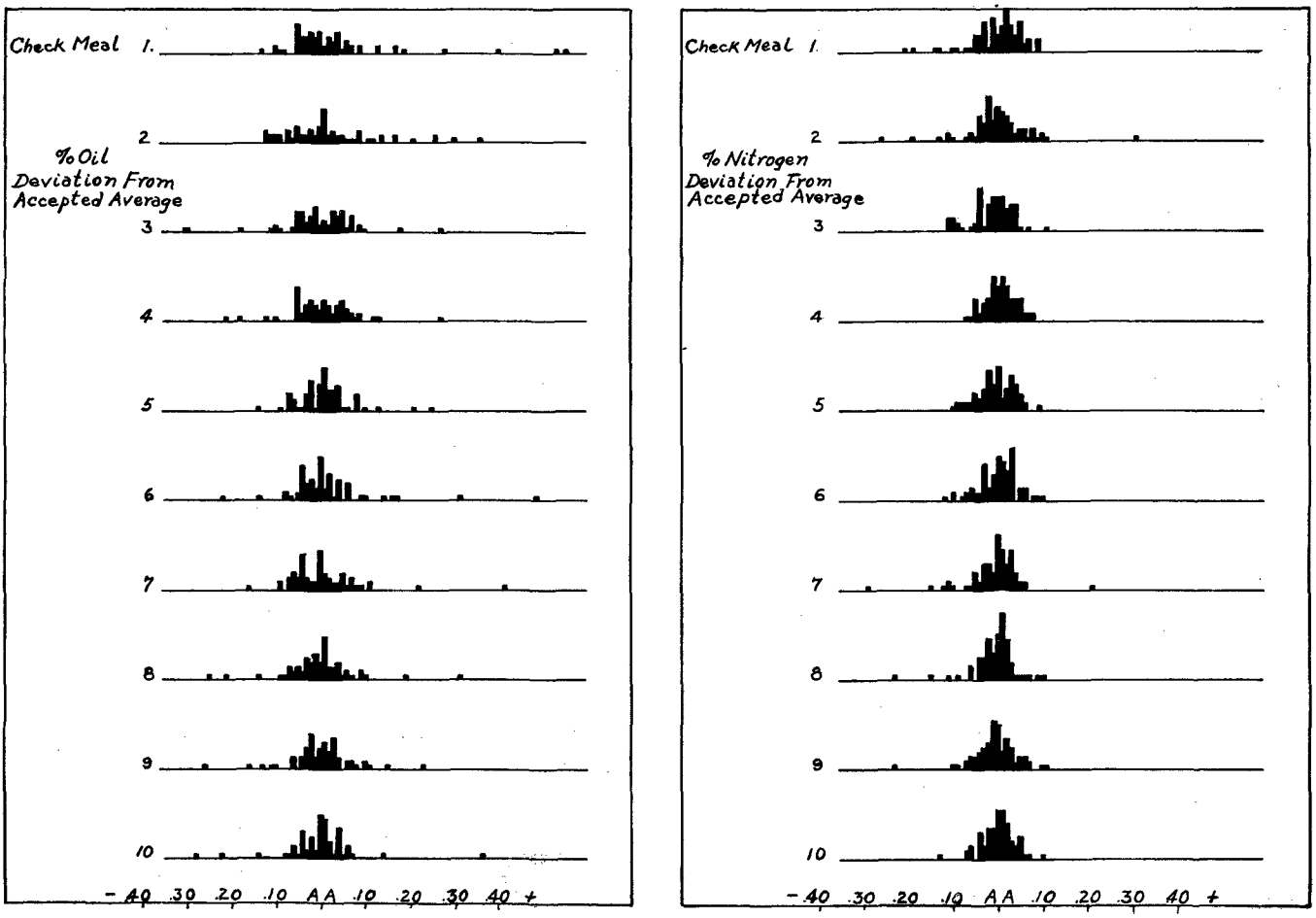
No critical study of the present method of arriving at the Accepted Average was made. The procedure has stood the test of time, and the histograms indicate its accuracy. Within the range of ±.12% deviation (see table) the Accepted Average appears a little low as higher results exceed lower results by 1 to 2%. However, if the Accepted Average is shifted .01% higher, a smaller number of results will appear within the .02% tolerance and the difference in percentage above and below becomes considerably wider.

In regard to the ±.02% tolerance now allowed in grading collaborators' reported results, it appears that this should not be uniform for both oil and nitrogen. It is obvious that oil is not regularly determined with as high a degree of precision. The standard deviation of .09% for oil is nearly double the .048% for nitrogen on samples 1 through 10. On nitrogen, 54.1% of 1,500 analyses were within the ±.02% tolerance while only 41.7% of the oils were so grouped. Increasing the tolerance to ±.03% for oil would include 54.9% of the reported analyses as compared with 54.1% within ±.02% on nitrogen. If the analyst who, by luck or by greater attention to every detail of the extraction procedure, shows few deviations outside the .02% tolerance for oil, he will have the advantage in winning the Smalley Cup for combined oil and nitrogen determination efficiency. A tolerance of .02% for nitrogen and .03% for oil appears to more nearly equalize the relative precision of the two determinations. (See Percent Within Tolerances Table.)

Examination of the histograms of results on individual Check Meals produces interesting conjecture. Quite frequently collaborators who have attained a high accuracy rating during the series and then miss an analysis by several points will blame their deviation on their sample portion. Sample preparation has been maintained at a very high level of excellence for which collaborators are indebted to Law and Company. It is questionable whether such aberrations are normal for the analytical technique or whether they derive from imperfect sample portions.

The individual histograms show clearly the greater spread of the oil results. Therefore the nitrogen results are more reliable as an indication of sample variation. Better still is a comparison of the two as to similarity of skewness and kurtosis, as the components of cottonseed meal are hulls of very low oil and nitrogen content and meats residue high in both. For example ,the narrowest deviation on nitrogen is shown on Sample 4, with high kurtosis. The oil, however, is peculiarly skewed with the largest single


% Oil
Deviation of Analyses
from Accepted Average
1500 Analyses
Series 1 thru 26
200
175
150
125
100
75
50
40
30
20
10
- .60 .50 .40 .30 .20 .10 A.A. .10 .20 .30 .40 .50 .60 +
% Nitrogen
Deviation of Analyses
from Accepted Average
1500 Analyses
Series 1 thru 20
- .60 .50 .40 .30 .20 .10 A.A. .10 .20 .30 .40 .50 .60 +


Check Meal 1.
2
% Oil
Deviation From
Accepted Average
3
4
5
6
7
8
9
10
- 40 .30 .20 .10 A A .10 .20 .30 .40 +
Check Meal 1.
2
% Nitrogen
Deviation From
Accepted Average
3
4
5
6
7
8
9
10
- 40 .30 .20 .10 A A .10 .20 .30 .40 +

group (8) at .05% below the accepted average. This is partially matched by a nitrogen group of 5 at .05% below the Accepted Average. Number 3, on both oil and nitrogen, shows split peakedness. Deduction indicates the probability that these Check Meals fell roughly into two groups of slightly different meats residue or hull proportion. This cannot, however, be considered conclusive on the basis of the 60 to 75 results reported. A certain similarity in the pattern of oils and nitrogens is apparent, particularly after allowance is made for greater spread of the former. But whether this is caused by sample portion variation or by normal scatter of analytical values has not been established.

From this incomplete statistical study of Check Meal results the following tentative conclusions are offered.

The method of obtaining the Accepted Average appears well justified.

Consideration should be given to increasing the tolerance on the oil determination to ±.03% to give parity with the nitrogen tolerance of ±.02%.

Standard Deviation Distribution and Percentages of Results About Arithmetic Mean

Check Meal	Oil				Nitrogen			
	Std. Dev.	% Below	% Within	% Above	Std. Dev.	% Below	% Within	% Above
No. 1	.13	4.7	87.5	7.8	.058	10.3	82.0	7.7
2	.11	11.1	74.6	14.3	.068	4.0	86.8	9.2
3	.09	8.1	88.7	3.2	.039	10.8	77.0	12.2
4	.07	6.6	85.2	8.2	.035	12.2	72.9	14.9
5	.06	12.7	74.6	12.7	.040	10.7	80.0	9.3
6	.09	7.9	88.9	3.2	.042	11.7	76.6	11.7
7	.08	6.5	88.7	4.8	.059	9.3	86.7	4.0
8	.08	7.9	85.8	6.3	.046	9.2	84.2	6.6
9	.07	6.3	85.8	7.9	.052	7.9	78.9	13.2
10	.09	3.2	92.0	4.8	.036	16.2	73.0	10.8
Avg.	.09	7.5	85.2	7.3	.048	10.2	79.8	10.0

Deviation Frequency Distribution Within ±.12 of Accepted Average 1,500 Oil and Nitrogen Results

	Oil			Nitrogen		
	No.	Dev.	No.	No.	Dev.	No.
	—		+	—		+
	117	.01	147	160	.01	169
	126	.02	94	138	.02	152
	105	.03	93	98	.03	120
	90	.04	88	67	.04	69
	72	.05	63	50	.05	58
	39	.06	42	36	.06	34
	35	.07	41	22	.07	21
	14	.08	19	10	.08	12
	12	.09	30	8	.09	12
	11	.10	11	16	.10	6
	5	.11	11	10	.11	3
	4	.12	5	4	.12	0
		Zero	4		Zero	
Total	630	141	644	629	192	656
		Total			Total	
	44.5%	1415	45.5%	42.6%	1477	44.4%

Percentage Within Tolerance of ±.02

Oil	Nitrogen
No. Results 625 41.7%	No. Results 811 54.1%

Percentage Within Tolerance of ±.03

Oil	
No. Results 823 54.9%	

The wider deviations on oil results may be due in part to nonuniformity in analytical detail such as oven drying of oil flasks and filter paper blank correction.

Check Meal sample preparation is very good but may possibly be further improved.

The work of L. M. Blaylock, Jr., and M. H. Fowler in compiling figures and calculating standard deviations is gratefully acknowledged.

Report of the Uniform Methods Committee Fall Meeting, 1946

Glycerine Committee:

The Glycerine Committee has made their report in which they recommend the adoption of three separate methods:

1. Apparent Specific Gravity by the Pycnometer Method at 25°/25° C.
2. Adoption of the determination of moisture by the Karl Fischer Method.
3. Determination of Glycerol by Oxidation with Periodic Acid.

The Uniform Methods Committee has approved all three of these for adoption as tentative methods.

Bleaching Methods Committee:

At the Spring Meeting the Uniform Methods Committee adopted the recommendations of the Bleaching Methods Committee, except that they felt there should be some method of determining when an oil falls into the class which requires activated clay for bleaching. Since that meeting considerable discussion has developed regarding this recommendation and the matter was again referred to the Uniform Methods Committee for reconsideration. It is now our recommendation that the report be accepted as originally given and that the question of when an oil is sufficiently green for the use of activated clay be left a matter of trading rules or agreement between buyer and seller.

Fat Analysis Committee:

The Fat Analysis Committee recommends a method for determining ash in fats and oils. The Uniform Methods Committee approves this method for tentative adoption.

They also recommend a method for the determination of moisture, acetone soluble and benzene insoluble in lecithin. The Uniform Methods Committee approves this for adoption as a tentative method.

They also recommend a method for the determination of refined and bleached color of tallow. The Uniform Methods Committee approves this for adoption as a tentative method.

They also recommend the use of carbon tetrachloride as an alternate solvent for washing in the determination on insoluble impurities. The Uniform Methods Committee approves this for adoption as a tentative alternate method for this purpose.

Color Committee:

The Color Committee makes recommendations as follows:

The method, which is soon to be published, reads as follows:

10. Weigh the refined oil and filter through the specified filter paper into a clean and dry container. Determine the color as directed in A.O.C.S. Official Method, Cc 13b-45. If a bleach test is required, it is determined on the filtered