THE ANALYTICAL CONSTANTS

OF

HORSE, NEATSFOOT, AND TALLOW OILS.

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COURSE X.

Among the gifts of nature to man, not the least import-
-ant from a utilitarian standpoint, are the oils. Derived, as they are, from so many and such varied sources, and applied to such a multiplicity of industrial and economic uses, they offer a field for investigation of no little interest. As lubricants, as textile agents, as preservatives of structures, as food, and as many other agents of human comfort, they have been studied with an eye to their best utilization. Oils, to speak broadly, are glycerides of the fatty acids: i.e. they are compounds of a fatty acid and glycerine. Glycerine, being a triatomic al-
-cohol, unites with three molecules of the acid. It is true that other elements enter into the composition of the various oils .....and these additional substances in some cases furnish a means of identifying the oil in which they occur,..... but the major portion of an oil consists of the glycerides of one or more of the many fatty acids. The diversity in the fatty acids occurring in the different oils, and the varying percentage com-
-position, of the oils, cause the various oils to exhibit dif-
-ferent phenomena, when subjected to various chamical and phys-
-ical tests. These differences offer a means of identification of the various oils: since a pure oil treated under standard con-
-ditions, will always give concordant results. This possibility of identification has commercial and possibly legal value. Ex-
-pensive oils are naturally, by unscrupulous dealers, adulter-
-ated with cheaper ones. The layman would be at loss to distin-
-guish between a pure oil, and a mixture: but the oil chemist, by virtue of his knowledge of the variations of the different oils, in their behavior under the above-mentioned tests can detect the presence of the adulterants, if such are used. ~~Cer-~~

Certain oils which are commonly met with have been very thorough -ly investigated, and their constants , as the expression of th -eir reactional behavior is called, have been definitely deter- -mined. Other oils, less commonly met with, have had less work done upon them: and their constants are, as yet, but imperfect- -ly known. The object of this discussion and its attendant expe -rimentation, has been to add to the general knowledge about ce -rtain of these comparatively uninvestigated oils. The oils chosen were neatsfoot, tallow, and horse. Let us first consid- -er these oils individually: and then make general comparisons.

NEATSFOOT OIL is a light yellow, bland, and fluid oil, obtained by boiling the feet of neat cattle. Five samples which we will call Nos. 1,2,3,4, and 5, were investigated. They were secured from various sources and it is believed, in most cases, are representative samples of pure Neatsfoot oil.

The first test applied was to obtain the Specific Grav- ity. This was effected by a Westphal balance, the oil being cool -ed to 15 °C. The results obtained are as follows:

Sample No.	Temperature.	Spec. Grav.
1	15°C.	0.915
2	15°C.	0.914
3	15°C.	0.919
4	15°C.	0.916
5	15°C.	0.916

Oil No. 2 was a much more yellow oil than the others, but it's constants show concordance and thereseems to be no reason to doubt it's purity. Oil No. 3, however, shows a marked variation in most of the constants determined, from the standard establish -edby the other samples examined, but as several special tests failed toshow the presence of certain possible adulterants, it

is included, although there is reason to believe it is not a pure oil. The next test applied, was the Valenta test. This consists in finding the temperature at which a certain amount of the oil dissolves in an equal amount of glacial acetic acid. The test was performed in this manner. Enough oil was poured into a test tube to fill about one inch of the tube. An equal quantity of 100% acetic acid was added. The test tube was then heated and stir-red until the oil and acid became a clear, homogeneous liquid. The source of heat was then removed, a thermometer inserted in the liquid, and the mixture allowed to cool. After a time, the clear liquid became cloudy, owing to the separation of the dissol-ved oil. The temperature at which this occurred was noted, and forms the Valenta test. This test is at best an approximate one, as the proportion of oil to acid causes a variation : and as in the commercial method the quantities are never accurately measured, a lack of concordance in this test is by no means a sign of adul-teration in the oil. The results obtained are :

SAMPLE NUMBER.	VALENTA.
1	70°C.
2	75°.5 C.
3	51°C.
4	61°.5 C.
5	75°.5 C.

Oils number 2 and 5 coincide exactly. Oil number 1 is a concordant result when the crudeness of the test is consid-ered. Oil number 4 shows a variation which is probably due to an error in the measurement of the quantities used . Oil number 3 is the oil that is doubtful: and its discrepancy is hardly within the error of manipulation: thus indicating again the probable presence of an adulterant.

The next test applied was the Maumené test and with it the Specific Temperature Reaction. The Maumene test depends upon the rise in temperature shown by an oil, on the addition of a certain quantity of Sulphuric acid. The Specific Temperature Reaction is the ratio between this result and the rise obtained by treating a corresponding weight of water with the same amount of acid. The test was applied in the following manner: A beaker of 150 cc. capacity was used and into this was weighed 50 grams of the oil. ~~was~~ The beaker and it's contents were then inserted in a calorimeter, consisting of an enamelled cup with an inner layer of cotton waste inserted between the cup and the beaker. This protects the beaker from draughts of air and maintains the uniformity of the temperature changes. To secure as much mechanical uniformity as possible the acid of 100% strength was placed in a 50 cc. burette with a glass stopcock and 10 cc. of the acid was allowed to run into the oil, drop by drop. The concordance of results obtained would seem to recommend this method. The oil is constantly stirred, during the addition of the acid with a 100 C. thermometer. With this the -mometer the initial and final temperatures are obtained and their difference gives the Maumene test. The results obtained are as follows:-

Sample No.	Temperatures. Initial.	Final.	Maumene.
1	24°.3	66°.5	42°.2
	24°.3	66°.5	42°.2
2	25°.2	67°.3	42°.1
	23°.7	65°.9	42°.2
3	24°.5	74°.0	49°.5
	24°.5	74°.0	49°.5
4	21°.0	63°.2	42°.2.
	22°.0	64°.2	42°.2

5	21°.7	63°.9	42°.2
	22°.7	64°.9	42°.2
H_2O	22°.0	70°.0	48°.0
	21°.8	69°.8	48°.0

Specific Temperature Reaction 87.9

It will be noticed that the above results are exactly concordant with the exception of No. 3 about whose purity suspicion has already been expressed. The Maumene test, while not a quantitive one, is a very reliable one qualitatively.

The next test applied is one of the most, if not the most illuminating, in regard to the nature of an oil. This test was performed in the manner recommended by Dr. A. H. Gill in his "Oil Analysis". The amount of oil used was from 0.3 to 0.5 grams. The results obtained were as follows:-

Sample No.	Iodine No.	Mean Value
1	73.1 72.8	72.95
2	72.9 72.9	72.90
3	66.8 67.4	67.10
4	72.1 72.2	72.15
5	65.6 66.4	66.00

Oils No. 1, 2, and 4 are practically the same. Oils No. 3 and 5 are concordant with each other and can be explained by the possi-bility of different processes being employed in the extraction of the oil.

The next test applied was the so-called titer test or the melting-point of the combined fatty acids. The fatty acids were

isolated as follows:-----Fifty grams of the oil were saponified on a water-bath in a 300 cc. Erlenmayer flask, with about 100cc. of strong alcoholic potash. A small funnel was placed in the ne -ck of the flask, to serve as a return-flow condenser. When the mixture became clear and homogeneous showing complete saponifi- -cation, it was removed , and allowed to stand for twenty-four hours. This gave the alcohol a chance to evaporate, and resulted in a more satisfactory final product than was secured when this step was omitted. At the expiration of this time distilled water to the amount of 150 cc. was added, and the whole mass boiled. When the mass was thoroughly fluid, hydrochloric acid (Sp. Gr. 1.12)wsa added, causing the separation of the fatty acids . The fatty acids thus liberated rise to the surface, in a yellow or a red layer. The acids are separated with a separatory funn -el, and washed three or four ttimes with hot water....cold water might cause a solidification of the less liquid acids,... to remove all traces of impurities. The acids are then run into an evporating-dish, and heated with absolute alcohol, on a water bath, to remove the traces of the wash-water. The combined fatty acids thus purified are run into glass-stoppered salt-bottles, and kept there for further use. The acids obtained from neats- -foot oil have a solid and a liquid portion: the latter being by far the greater part. The liquid part is Oleic acid: and the solid,chiefly Stearic acid . The apparatus for the titer test consists of a 100cc. round-bottomed flask, forming an air chamber for a five-inch test tube which fits exactly the neck of the flask. The test is applied in the following manner: ---The fat -ty acids are heated on the water bath, until they form a clear homogeneous liquid. This is poured into the test tube, a ther- -mometer is inserted, and the liquid gently agitated, to keep

the temperature uniform. The liquid suddenly becomes cloudy, and inside the space of 1°C. fall in temperature, goes from a perfectly clear fluid to a translucent or even opaque liquid. The results obtained are as follows:

SAMPLE NUMBER.	SOLIDIFYING POINT C.
1	20°---19°
2	19°---18°
3	18°---17°
4	16°
5	26°.5---25°.5

The seeming lack of concordance is explained by the varying amount of Stearic acid present. Oil number 5 which is so widely at variance with the rest was solid at room temper-ature: showing the presence of much Stearic acid. This test is a fairly valuable one: it being a great help in the detection of tallow oil as an adulterant of neatsfoot oil. The next and last test applied to the oil, was to secure the Iodine Number of the fatty acids. This was conducted in exactly the same man-ner as in the case of the oils themselves: except that the fat-ty acids were heated to the point of fluidity , to insure the uniformity of the samples taken. The results were as follows:

Sample No.	Iodine No.	Mean Value.
1	69.3 68.2	68.65
2	65.4 63.8	64.60
3	66.9 67.7	67.30
4	68.8 70.1	69.5

63.6

5 63.55

63.5

There seems a lack of concordance in these results which may be attributable to the varying percentage of the different fatty acids.

These results will all be discussed later in connect-ion with the constants determined for the other oils. The next oil to be considered is Tallow Oil.

TALLOW OIL is a bland, light- yellow oil, changing to a solid white fat at ordinary room temperatures. At the temperatures at which it is liquid, it greatly resembles Neatsfoot oil in appearance and it is used to adulterate it. It is obtained by pressing tallow in upright screw presses at about 8000 lbs. to the square inch. The constants determined, and the methods for obtaining them, are similar to those used in the investigation of the Neatsfoot oil.

The Specific Gravity was obtained at 100°C. instead of 15°C. in order that the Westphal balance might be available. The results obtained are as follows:-

Sample No.	Specific Gravity at 100°C.
1	0.794
2	0.794
3	0.794

These results show a very gratifying concordance which is repeated in all the results upon Tallow oil.

The Valenta test was next applied and gave the following resul

Sample No.	Valenta.
1	73°.50
2	71°.00
3	75°.75

These results again show a concordance, the variation being within the error of the experiment. The Maumene test was next carried out, with the following results:

Sample No.	Temperatures. Initial.	Final.	Maumene.
1	30°.0	65°.0	35°.0
	29°.0	64°.0	35°.0
2	27°.0	62°.0	35°.0
	27°.0	62°.0	35°.0
3	25°.0	60°.0	35°.0
	25°.0	60°.0	35°.0
Specific Temperature Reaction			72°.9

The above results are again perfectly concordant.

The Iodine Number, which was next determined, gave the following results:-

Sample No.	Iodine No.	Mean Value.
1	55.7	55.8
	55.9	
2	56.2	56.55
	56.9	
3	56.7	56.75
	56.8	

Again the results are concordant, and would point to a uniform method of procuring the oil. The titer test was carri-ed out on the combined fatty acids extracted by the same meth--od used in the extraction of the fatty acids from the neatsfoot oil. The oil is probably largely stearin, with some olein. The fatty acids are solid at room temperature, and are a light yel--low brown in color. The results secured, follow:

SAMPLE NUMBER.	SOLIDIFYING POINT °C.
1	36°...35°
2	37°.5...36°.5
3	35°.5...34°.5

These results are again concordant. The Iodine Number of the fatty acids was conducted in the usual manner: great care being taken that the acids should be liquid and homogeneous. The results obtained concur with those secured from the oils.

Sample No.	Iodine No.	Mean Value.
1	54.6	54.6
	54.6	
2	57.2	57.0
	56.8	
3	56.6	56.6
	56.6	

The tallow oils showed an unusual concordance , and coming as they did from widely different sources, speak well for the purity that these oils attain. The last oil to be considered is the horse oil. This presents the most interesting problem of the three kinds investigated. First, because less work has been done on this oil than on either of the others. Second, the samples varied so widely among themselves. Of this oil five samples were examined. They were so diverse that a brief account of their appearance will not, it is hoped, be out of place.

Oil number 1 was a whitish-brown oil, semi-fluid, the stearin being granular. When the oil was poured on a cloth and the cloth then pressed, the liquid portion passed into the fibre of the cloth, leaving the stearin as a white cake. Oil number 2 was a dirty dark brown oil, semi-liquid, but absolutely homogeneous. Six hours' constant centrifuging on a diameter of ten inches and fifteen hundred revolutions per minute, failed to separate a liquid portion. Some mechanical dirt was also present. Oil number 3 was the most liquid of the samples handled

Its color was golden, yellow-brown. It separated, on standing, into a clear red-brown oil, and yellowish stearin. The stearin was granular, as in oil number 1: but the granules were much smaller. Oil number 4 was a golden brown, with a pinkish reflection: a very smmoth; homogeneous oil: the most nearly a solid, of all the samples examined. Oil number 5 was a modification of oil number 4: it having all the distinctive properties of oil number 4, but in a modified form.

These oils were subjected to the same tests as the neatsfoot and the tallow oils: and then a separation of the sol -id and liquid portions was made, and the Iodine Number of the liquid ascertained.

The first test applied was, as in the other cases, to ascertain the specific gravity of the oils. Three were deter -mined at 15°C. in a picnometer: but in only one case, is there reason to believe that the correct specific gravity was obtained. These oils should be again determined at 100°C., as were the ot -her two samples. Injury to the Westphal balanceprevented this being done. One of these samples ,---number 5,----came from a single horse: the others,so far as could be ascertained, were drawn from general supplies. The specific gravities found, are as follows:

Sample No.	Temperature °C.	Specific Gravity.
1	15°	0.919
2	15°	0.916
3	15°	0.922
4	100°	0.798
5	100°	0.799

No's. 2 and 3, as already stated, should be tried again, at 100°C. The Valenta test, the next one applied, speaks for itself. It is

as follows:-

Sample No.	Valenta
1	80°.25
2	54°.00
3	71°.00
4	48°.00
5	61°.00

It can be seen at a glance of the above list that, so far as a means of identification of Horse oil is concerned, the Valenta test has absolutely no value. Particular care was taken to keep the con-ditions and quantities as nearly uniform as was possiblevwithout exceeding the commercial accuracy of the test. The result is a range from 48.0 C. to 80.25 C. Also the more solid fats have the lower Valenta point which is exactly the reverse of what one would expect to be true. The next test, the Maumene, shows less divergence, but still exhibits a certain discrepancy. The results are:-

Sample No.	Temperatures. Initial.	Final.	Maumene.	Mean Value.
	22°.4	70°.2	47°.8	
	23°.7	69°.7	46°.0	
1	23°.3	70°.0	46°.7	46°.0
	23°.0	68°.0	45°.0	
	23°.5	68°.0	44°.5	
2	23°.2	74°.0	50°.8	52°.15
	23°.5	77°.0	53°.5	
3	23°.8	78°.8	55°.0	54°.75
	24°.5	79°.0	54°.5	
4	24°.7	80°.2	55°.5	54°.25
	25°.0	78°.0	53°.0	
5	21°.0	74°.5	53°.5	53°.5
	21°.3	74°.8	53°.5	

The Specific Temperature Reaction, in this case, cannot be assigned a single value but must be given in limiting values. Those value which it has been deemed best to assign as limits are here given The reason for their selection will be given later.

Specific Temperature Reaction 95.8 ....112.0

Oils No. 4, 2, 3, 4, and 5show a fair concordance i.e. from 52.55 to 54.75. OilNo. 1 seems to be absolutely discordant, since a mean of a number of trials shows the result as 46.0. The only explanation that can be offered is, that portions of the horses ~~we~~ were used in making this oil that were not used in making the ot-her oils, or Visa versa. The next test was the Iodine Number and the results are here appended:-

Sample No.	Iodine No.	Mean Value.
1	74.4 75.9	75.15
2	83.6 81.4	82.5
3	86.6 85.9	86.3
4	80.0 79.9	79.95
5	79.3 78.3	78.8

The discrepancy noticed, upon inspection, between the results obtained from the same oil, may be explained by the fact that the oil was weighed cold. While these differences are not great, it is probable that they could be reduced by weighing the oil after ~~hs~~ heating and stirring to secure a greater homogeneity of the sample As for the mean results, Oil No. 1 is again an unexplained variant unless the previous explanation is allowed. No's. 4, 2, and 3 are

measureably of the same consistency and the results a concordance relative to their degree of fluidity. This also explains why No. 3, by far the most liquid of all the oils, showed the otherwise dis cordant result of 86.3. The titer test, as the next one applied, brings in it's turn a problem. The table is here given:-

Sample No.	Titer
1	33°.5....32°.5
2	31°.0 ...30°.0
3	26°.0 ...25°.0
4	31°.0 ...30°.0
5	35°.0 ...34°.0

No. 3, the lowest, is the most liquid oil and No. 5, avery solid oil, is the highest. But No. 4 and No. 2 form a mean between No's 3 and 5 and No. 4 is nearly as solid as No. 5. Still, this could be possible, were it not for the fact that No. 1, a fluid oil, comes aboveNo's. 2 and 4 which are much more solid. It is evident that, unlessthe first premise of difference in fats is admitted, an insurmountable discrepancy exists. Assume it to be true, however, and the samples arrange themselves in a fairly systematic way. The Iodine Number of the fatty acids was next secured, as another way of getting additional data upon these varying samples. The results are:-

Sample No.	Iodine No.	Mean Value.
1	72.4	72.9
	73.4	
2	71.3	72.35
	73.4	
3	78.5	78.7
	78.9	
4	79.7	80.4
	81.1	

80.8

5 82.15

83.5

These give one more proof of the theory: except that number 2, which, up to this time, has been showing good results, now gives an Iodine Number below that of number 1: which would otherwise be the lowest. The explanation might be that although the greatest care was taken in isolating the fatty acids, some difference in treatment may have caused the acids of this oil to polymerise or otherwise change their structure, so that their number of bonds available for iodine saturation was de--creased. This is, of course, the purest conjecture: but it offers a possible solution to the problem.

Feeling that these preceding results while, in most cases, satisfactory, and measurably consordant, were open to yet further illumination, it was decided to separate the solids and liquid portions and to see if the results obtained gave ad--ditional proof of any of the theories previously advanced. It was first necessary to devise some means of making this separat--ion . The commercial method, the screw-press, being unavailable the following laboratory method was devised. About 100cc. of the oil were placed in the tube of a centrifuge. The sample was the heated to about 95°C., at which temperature it was extremely fluid. The tubes were then placed in an electric centrifuge, and rotated at a rate of 1500.r.p.m. for a period of about two hours. At the end of this time the oil gradually cooling, had slowly precipitated its solid portion: and this as fast as it separated from the liquid, was caught by centrifugal force and packed at the expreme end of he tube. Thus a clear, transparent oil was obtainable from specimens that at the end of six hours cold centrifuging showed an undiminaished homogeneity. After the clear supernatant liquid was poured off, the solid portion

could be removed intact by cutting it out with a knife. The liquid portion was then examined as to its Iodine Number with the following results:

Sample No.	Iodine No.	Mean Value.
1	No separation made.	
2	81.97	82.04
	82.11	
3	83.13	83.69
	84.25	
4	80.70	81.85
	83.00	
5	78.41	78.19
	77.97	

Number 1, the oil most desired for this test, was not av--ailable, as in spite of its granular composition, and semi-fluid consistency, it was impossible to make a separation of the two portions. Numbers 2,3 and 4 show good, concordant results: and number 5 although a little lower than might be expected, is not an impossible value. On the whole, the changing ratio of solid to liquid as might be expected, has its effect upon the constants of the oil. Number 1 showed, uopn further use, that there were present, in it, certain particles of a membranous nature , which might easily be a portion of one of the intestines. This, again pounts to the theory of the various origins of the fats, and also points to the use of the viscera of the animal as one source of the fat in oil number 1.

Now to turn to a comparison of the three oils, and their several constants. Neatsfoot oil is of course the most expensive, and it is as an adulterant to it, that the others would be applied. How could they be distinguished, if so applied?

The tallow oil would be soluble in the neatsfoot oil: but how the specific gravity would be affected cannot be foretold with--out further data. The horse oil has practically the same speci-fic gravity as the neatsfoot, and thus could detection by that test. The Valenta test as has already been said, is practically useless. It would be a comparitively easy matter to find a horse oil that would give the same figures that are usually ascribed to neatsfoot: and both the tallow and the neatsfoot show several values around 70 C., so that tallow oil could be used with impu-nity, so far as this test is concerned. The Maumene test at first sight, seems to show a wide variation and thus to present a means of detection . But it would not be difficult to mix an oil giving 35°C. with an oil giving 55°C. in such proportions as to give a mixture giving 42°C., and thus, in the mixture, an adulterant is obtained secure from detection by the Maumene teat. With the Iodine Numbers the same proposition is presented Tallow oil gives, roughly, 56, and horse oil rougly, 80. These could be combined, to give an oil running from 67 to 72. The titer test gives the first solution of the difficulty. Neatsfoot oil generally runs from 20°C. down: if the specimens examined are fair samples-----and there is every reason to believe that they are,----while tallow at 36°C. and horse oil at 30°C. upward, are thus hardly likely to escape detection. The Iodine Number of the fatty acids offers the same objection as the Iodine Number of the oils themselves. But the case is not as hopeless as it at first appears, with its one test , the titer test, by which adulteration can be detected. A mixture that would give the right Maumene test, would probably give anything but the correct Iodine value: and therefore by applying the last four

tests to a neatsfoot oil, the presence of the others could undoubtedly be detected.

While these results are by no means absolutely concl-usive, and while further work along these lines would be of indubitable value and interest, an attempt has yet been made to conduct these few tests in such a manner, and under such condi-tions, that under similar conditions,----and these are hot dif-ficult to secure,----concordant results could be obtained from oils of the same nature as those examined. Also an attempt has been made to bring the accuracies of the laboratory to the ser-vice of certain commercial needs. How far this has been accom-plished this is not the place nor the time to decide. It is to be hoped, however, that the results set down in the foregoing pages may prove a little profitable, from the commercial stand-point, as tending to the establishment of a fair standard of purity in a standard article of commerce: and from the scien-tific standpoint, as achieving one more approxiamtion to an exact truth.