THE DETERMINATION

of the

REICHERT-MEISSL NUMBER AND THE POLENSKE NUMBER

of

BUTTER FAT, COCOANUT OIL AND DEFINITE MIXTURES OF THE SAME.

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A thesis

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by

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Determination of the Reichert-Meissl Number and Polenske Number of butter fat, cocoanut oil, and definite mixtures of the same.

The object of these determinations was to find the percentage of soluble and insoluble volatile acids in butter fat, cocoanut oil, and their definite mixtures.

The Reichert-Meissl Number is the determination of the soluble acids, and the Polenske Number of the insoluble acids. Caprylic and caproic acids dissolve almost completely at a temperature of 15°C., while capric is almost insoluble in cold water, therefore, the Reichert-Meissl Number represents chiefly the first two acids, and the Polenske Number the last.

For many years chemists worked on methods for the determination of these acids in different fats, especially in butter fat and cocoanut oil.

In 1879 Reichert made the first determination of the insoluble volatile acids that was at all satisfactory. In a series of experiments he obtained results which checked very closely. In the next few years many modifications of his

method were offered, but the only one that he would consent to inaugurate with his own was the one made by Meissl about one year after Reichert's method was generally accepted, and is now known as the Reichert-Meissl method. Many criticisms were made upon the Reichert process on account of the indefiniteness of some of the statements. From these one could not tell exactly when the saponification was complete; when the alcohol was removed; nor when the acids were completely liberated. Meissl was much more specific throughout in writing up his process.

The Reichert Number is the number of cubic centimeters of tenth normal sodium hydroxide solution required to neutralize the soluble volatile acids obtained from 2.5 gms. of fat when treated by the Reichert process as given below.

The Reichert-Meissl Number is the number of cubic centimeters of tenth normal sodium hydroxide solution required to neutralize the soluble volatile acids obtained from 5 gms. of fat when treated by the Reichert-Meissl process as given later in this paper.

Original Reichert Method. Zeit. für An. Chem. Vol. 18, p. 69.

Two and five tenths grams of fat freed from water and filtered through cotton, is weighed into a flask of about 150 c.c. capacity, preferably an Erlenmeyer flask, and 1 gram of pure potassium hydroxide and 20 c.c. of 80 o/o alcohol are added.

This mixture is then heated on a water bath with frequent shaking till it is no longer a smeary mass. Fifty cubic centimeters of water is then added, and when the soap is dissolved, 20 c.c. of dilute sulphuric acid (1 c.c. pure sulphuric acid in 10 c.c. water) is added. The flask and condenser are then connected by means of a spherical tube with a large opening to prevent the sulphuric acid from passing over, and a current of air passed through to prevent bumping.

The distillate is collected in a flask graduated to 50 c.c. and filtered through a moist filter paper. After 15 or 20 c.c. has passed through, it is returned to the distilling flask and exactly 50 c.c. distilled over, passing it through the moist filter paper.

After four drops of litmus is added as an indicator, titrate the filtrate with a tenth normal solution of sodium hydroxide. The color must remain after standing a long time.

Reichert obtained the following results on butter fat and cocoanut oil:

	Butter fat	Cocoanut oil
No. 1	14.5	3.70
No. 2	14.45	3.70
No. 3	14.6	

Meissl's Modification of the Reichert Process.
Zeit. für An. Chem., Vol. 23, p. 564.

Five grams of pure filtered fat is weighed into a flask of about 200 c.c. capacity. Two grams of strong potassium hydroxide and 50 c.c. of 70 o/o alcohol are added. The mixture is heated on a water bath with frequent shaking till the oily drops on the surface disappear. It is then evaporated to dryness. One hundred cubic centimeters of water is added and the mass dissolved. Forty cubic centimeters of dilute sulphuric acid (1:10) and some small pieces of pumice stone are then added.

The flask is connected to the condenser by means of a spherical tube with an elbow joint and the distillation continued about an hour. The distillate is received in a 110 c.c. graduated flask. The distillate is thoroughly mixed, and 100 c.c. is titrated with a tenth normal sodium hydroxide solution, using litmus as an indicator. The titration is continued until the color remains after repeated shaking.

With forty-nine samples, Meissl found that the number of cubic centimeters of sodium hydroxide varied from 27-31.8.

Bulletin Method for the Determination of the Reichert-Meissl Number. U.S.Bulletin No.107,(revised) Bureau of Chemistry.

The butter or fat is melted at about 60° for two or three hours, or until the water and curd have separated. The clear fat is poured through a dry filter, a hot water funnel being used. If the filtrate is not clear, it is filtered again.

The saponification flasks are thoroughly washed with water, alcohol, and ether, wiped dry on the outside, and dried

for an hour at the temperature of boiling. They are then cooled and weighed.

Seven and seventy-five hundredths cubic centimeters, about 5 gms.,of thoroughly mixed fat is measured into the flask with a pipette that has been warmed to about 50°C. This is allowed to stand 15 to 20 minutes and is then weighed.

Ten cubic centimeters of 95 o/o alcohol is poured into the flask containing the fat, 2 c.c. sodium hydroxide solution (1:1) is added, and the flask is then connected with a reflux condenser, and heated on a steam bath until saponification is complete. After saponification, the alcohol is removed by dipping the flask into a steam bath up to the neck. When the alcohol is nearly gone, frothing may occur. Any loss from this cause or creeping up the sides of the flask is avoided by removing the flask from the bath and shaking to and fro. The last trace of alcohol is removed by waving the flask briskly, mouth down, to and fro.

The soap is then dissolved by adding 135 c.c. of recently boiled water, and warming on a water bath, with

occasional shaking until the solution is clear. It is then cooled to from 60° to 70° and 5 c.c. dilute sulphuric acid (1:4) is added. It is stoppered and heated on a water bath until the fatty acids form a clear, transparent layer on top.

The contents are then cooled to room temperature, a few pieces of pumice stone are added, and the flask is connected with the condenser. It is heated slowly with a naked flame until ebullition begins, it is then distilled, regulating the flame so that 110 c.c. will distill in 30 minutes.

This distillate is mixed, filtered through a dry filter, 100 c.c. titrated with a tenth normal barium hydroxide solution. The titration is continued until the color remains unchanged after two or three minutes.

Calculation:

The number of cubic centimeters of the tenth normal barium hydroxide solution is increased by one tenth, the result is divided by the weight taken and is then multiplied by five.

Polenske Method. Analyst, Vol. 29, p. 154.

To 5 gms. pure fat are added 20 gms. glycerol and 2 c.c. of 50 o/o sodium hydroxide solution, care being used to avoid an alcoholic solution of the sodium hydroxide.

Saponification is completed by the usual method for the determination of the Reichert-Meissl Number. After this is dissolved, the requisite amount of sulphuric acid is added.

After the condenser is connected, the flow is regulated so that 110 c.c. of the distillate is passed over in from nineteen to twenty-one minutes. The temperature of the condenser was between 18^{0} and 20^{0}. When the 110 mark on the receiving flask is reached, it is replaced by a 25 c.c. cylinder. The receiver is placed in a water bath at a temperature of 10^{0} for ten minutes, the surface of the water being just above the 110 mark, the contents not being mixed. The insoluble acids rise into the neck of the flask, and in the case of butter, solid, white opaque granules are formed, while with pure cocoanut oil, clear, oily drops are obtained. Mixtures containing more than 10 o/o of cocoanut oil also yield oily droplets.

After the contents are mixed and filtered, the Reichert-Meisl number is determined on the filtrate.

The condenser, cylinder, and receiver are washed with 18 c.c. of water, all the wash water is then poured over the filter. The insoluble fatty acids on the filter are dissolved in alcohol, and the solution is titrated with barium hydroxide, phenolphthalein being used as indicator.

The number of cubic centimeters of tenth normal barium hydroxide solution required, is termed the "new butter value", or Polenske Number of the fat.

Thirty-one samples of butter having Reichert-Meissl values of: 23.3-30 gave Polenske Numbers of 1.5-3.
From a number of other analyses when the Reichert-Meissl values were from:

(1) 23-27 the Polenske Numbers were 1.6-1.9
(2) 28, 29, 30 " " " " 2.2, 2.5, 3

The results obtained from four determinations on cocoanut oil were: Reichert-Meissl values 6.8-7.7, Polenske Number 16.8-17.8.

In case (1) a rise of 1 in the Reichert-Meissl value gave a rise of .1 in the Polenske value, while in case (2) the rise in Polenske value is greater, and it is still more marked if cocoanut oil be present; the greater the percentage of cocoanut oil, the more marked is the change.

The method used in obtaining the data on the Reichert-Meissl Number given in this paper is as follows:

Melt the butter at about 60° for two or three hours, or until the water and curd have separated. Pour the clear fat through a dry filter, using a hot water funnel. If the filtered fat is not clear, filter again.

Wash the saponification flasks thoroughly with water, alcohol, and ether, wipe dry on the outside, dry for an hour at the temperature of boiling water, cool and weigh.

Measure 7.75 c.c., about five grams of the thoroughly mixed fat into the flask with a pipette that has been warmed to about 50° C. Allow to stand fifteen or twenty minutes and weigh.

Place 10 c.c. of 95 o/o alcohol in the flask containing the fat, add 2 c.c. of sodium hydroxide solution (100 gms. pure

sodium hydroxide in 100 gms. distilled water). Using a glass tube at least a meter long in a rubber stopper for a reflux condenser, saponify at least half an hour on a steam bath, being careful to keep the solid contents covered with the alcohol.

After saponification, remove the alcohol by evaporating to dryness on a steam bath, a card may be inserted to hasten the evaporation.

Dissolve the soap by adding 135 c.c. of recently boiled water and warm on the water bath till the soap is dissolved, cool to 60° or 70°, add five c.c. of dilute sulphuric acid (200 c.c. pure concentrated sulphuric acid in a liter of water), connect with the same reflux condenser, heat on the water bath till the fatty acids form a clear, transparent layer on top. Cool to room temperature, add a few pieces of pumice stone to prevent bumping, connect with a condenser, heat slowly at first, the flask resting on a wire gauze, after ebullition begins, regulate the heat so that 110 c.c. will pass over in about thirty minutes, using a flask graduated at 110 c.c. for the receiving flask.

Filter this distillate through a dry filter, keeping it at about 15°. Wash the condenser and receiving flask three times with recently boiled water cooled to about 15°, using about 15 c.c. each time.

Titrate the 110 c.c. filtrate with tenth normal solution of sodium hydroxide, using phenolphthalein as indicator, the color must remain two or three minutes.

The number of c.c. sodium hydroxide used in the titration is taken as the Reichert-Meissl Number.

Comparison of the three methods.

	Reichert	Reichert-Meissl	Bulletin
Fat	2.5	5	5
Alkali	1 gm.KOH	2 gm.KOH	2 c.c. NaOH Sol.(1:1)
Alcohol	20 c.c. 80 o/o	50 c.c.70 o/o	10 c.c.95 o/o
Water to dissolve	50 c.c.	100 c.c.	135 c.c.
Sulphuric acid	20 c.c. (1:10)	40 c.c	5 (1:4)
Distillate	50 c.c.	110 c.c. titrate 100 c.c.	110
Time of distillation	Not stated	1 hr.	30 min.
Alkali	NaOh	NaOH	BaOH
Indicator	Litmus	Litmus	phenolphthalein

The method used in obtaining the data on the Polenske Number given in this paper is as follows:

After the last drop of wash water passes through the filter paper in the determination of the Reichert-Meissl Number, wash the condenser and receiving flask with three successive 15 c.c. portions of 90 o/o aldehyde-free alcohol. Pour these washings through the filter and finally wash the filter paper with 2 or 3 c.c. of the fresh alcohol.

Titrate alcoholic washings with a tenth normal sodium hydroxide solution using about.5 c.c. of phenolphthalein as indicator. Continue the titration until the color remains two or three minutes after shaking thoroughly.

The results obtained by the above methods are as follows:

Grams	C.C.NaOH	R-M No.	Butter fat	C.C.NaOH	Polenske No.
5.312	29.1	27.88	Fats dried		Not found
5.	27.8	28.297	" "		"
5.192	28.3	27.741	" "		"
5.007	31.4	31.921	" "		"
5.061	31.3	31.475	" not dried	1.5	1.508
5.019	32.1	32.626	" " " (Different sample)	2.4	2.433
5.384	30.75	29.066	" " dried		Not found
5.048	27.05	27.273	" " "	1.6	1.613
5.106	26.7	26.616	" " "	2.1	2.093
5.227	28.35	27.606	" " "		Not found
5.013	26.	26.397	" " "	1.7	1.726
5.0363	27.6	27.892	" " "	2.	2.021
5.0473	27.2	27.428	" " "	1.95	1.966
5.002	27.65	28.136	" " "	2.7	2.748
5.024	27.5	27.914	" " "	1.5	1.520
5.114	29.65	29.508	" " "	1.6	1.592
4.978	29.6	30.262	" " "	1.55	1.585
4.768	29.7	30.61	" " "	2.5	2.577
4.702	29.3	30.618	" " "	2.4	2.508
5.086	31.8	30.722	" " "	2.6	2.512

Butter fat and cocoanut oil.

Grams	C.C.NaOH	R-M No.	90 o/o butter fat, 10 o/o cocoanut oil.	C.C.NaOh	Polenske Number.
5.3115	29.9	27.356		3.2	3.067
5.104	28.5	28.420		4.3	4.388
5.286	28.2	27.152		1.8	1.733
5.4337	28.5	26.691		1.9	1.780
5.277	28.1	27.103		1.6	1.543
			80 o/o butter fat, 20 o/o cocoanut oil.		
5.005	25.6	26.		3.7	3.762
5.026	24.7	25.		4.1	4.151
5.068	24.7	24.87		3.4	3.415
5.011	24.6	24.984		3.	3.047
5.056	25.9	26.073		4.8	4.843
			70 o/o butter fat, 30 o/o cocoanut oil.		
4.811	23.45	23.95		4.2	4.290
4.858	24.15	24.426		5.15	5.209
4.988	23.95	24.432		5.7	5.816
5.086	24.35	24.368		4.5	4.503
			60 o/o butter fat, 40 o/o cocoanut oil.		
4.946	22.	21.858		5.25	5.216
4.976	23.	22.715		5.35	5.284
4.990	22.7	22.353		5.15	5.071
			50 o/o butter fat, 50 o/o cocoanut oil.		
4.939	20.95	20.843		5.7	5.671
4.933	20.95	20.871		7.75	7.720
4.961	20.8	20.601		6.05	5.992

Butter fat and cocoanut oil

Grams	C.C.NaOH	R-M No.	40 o/o butter fat, 60 o/o cocoanut oil.	C.C.NaOH	Polenske Number
5.059	18.8	17.044		8.5	8.257
5.041	18.3	17.838		7.5	7.311
5.112	17.6	16.883		6.7	6.423
5.204	19.35	17.858		6.7	6.327
			30 o/o butter fat, 70 o/o cocoanut oil.		
4.890	17.25	17.375		10.1	10.5
4.841	16.5	16.748		12.2	12.383
5.570	17.9	15.80		7.8	6.885
			20 o/o butter fat, 80 o/o cocoanut oil.		
4.700	15.45	16.153		10.05	10.57
5.041	16.95	16.253		10.08	9.826
5.053	15.75	15.675		7.85	7.635
			10 o/o butter fat, 90 o/o cocoanut oil.		
5.061	14.1	13.69		9.9	9.612
5.113	13.55	13.023		7.8	7.496
5.022	13.4	13.111		10.3	10.78
			100 o/o cocoanut oil.		
5.1823	10.1	9.577		10.9	10.333
5.100	10.2	9.827		10.4	10.011
5.125	10.6	10.161		13.8	13.308
5.215	10.8	10.176		12.9	12.155
5.151	11.85	11.303		13.3	12.686
9.165	10.95	10.417		13.6	12.938

The Meissl modification greatly improved the Reichert process, yet there are still many chances for errors to be made in the carrying out of the determination.

The method used in obtaining the above results is a slight modification of the one given in Bulletin No. 107 (revised) Bureau of Chemistry. Even with this method the following errors are possible:

1. The insoluble acids may hold the soluble ones.
2. Carbon dioxide may be absorbed.
3. Ethers may be formed during saponification.
4. Ethers may be formed during distillation.
5. The shape and size of the distilling flask may affect the results.
6. The position of the condenser may cause large quantities to collect on the wall.
7. Method of applying heat and its intensity may cause the breaking up of other acids.
8. Time of distillation may make a difference.

9. Temperature of distillate during filtration may affect the relative quantities of soluble and insoluble acids.

10. Cohesion of fatty acids during distillation.

All the errors that may occur in the Reichert-Meissl determination may also affect the Polenske Number, and in addition the following errors may occur:

1. Appreciable quantities of the insoluble acids collect in the tube connecting the distilling flask and condenser.

2. The condition and size of pumice stone greatly affect the results as shown by:

(a) Tatlock and Thomsen - Jour. Sc. of Chem. Ind. Vol. 29, p. 792.

On the same samples of butter fat they found the conditions:

		Pol. No.(A)	Pol.No.(B)
2 small lumps	pumice stone	2	-
.1gm. No. 1	" powder	2.3	3.7
.1 " " 2	" "	2.5	4.1
.5 " " "	" ""	2.75	4.4
1.0 " " "	" "	2.9	-

(b) A. Hesse.- Jour. Sc. Chem. Ind. Vol. 24, p.251. found that if 2 mm. pieces be used, acids distill which would otherwise remain in the flask. He also states that the Polenske Number should be .8 higher than Polenske gave it.

3. Mode of applying heat greatly affects results, even more than it does the Reichert-Meissl Number.

In order to avoid some of these errors Woolny says a flask of about 300 c.c. capacity should be used, with the neck 7 to 8 cm. long and 2 cm. across, and that 2 c.c. of 50 o/o sodium hydroxide solution and 10 c.c. of 96 o/o alcohol should be taken.

It is necessary to use great caution with the Polenske determination. After the distillate from the butter has been filtered it should be perfectly clear, while the filtrate from the cocoanut oil will be milky, providing each is filtered at about 15°C. The insoluble acids in the case of butter are crystalline, while those of the cocoanut oil form little drops on the surface of the distillate, and unless the filter is wet before these drops come in contact with it, some of them will pass through.

In washing the condenser and receiving flask, the alcohol must be free from aldehyde in order to determine the end point.

Not all chemists agree with Polenske that there is a definite relation between the soluble and insoluble volatile acids in butter and cocoanut oil. Tatlock and Thomsen give the following results upon several determinations:

	Reichert-Meissl Number	Polenske Number
Butter fat	28.1	1.8
Cocoanut oil	7.5	18.
10 o/o co.oil, 90 o/o b. fat	27.5	2.4
20 o/o " " 80 o/o "	24.4	4.2
30 o/o " " 70 o/o "	22.5	5.7
40 o/o " " 60 o/o "	20.9	7.4

This also shows that the soluble volatile acids in these mixtures are higher and the insoluble lower than the average of those given by the butter fat and cocoanut oil separately.

These chemists also say that some of the insoluble acids are insoluble only under certain conditions, and that if a large quantity of water is used, the number for the soluble increases and the number for the insoluble decreases. If the distillation is carried to 500 c.c., the Reichert-Meissl value becomes 36, which is 28.1 under the usual process. In the case of the cocoanut oil, when 500 c.c. of the distillate is obtained, the Reichert-Meissl Number becomes 28, whereas the

value with the usual process is 7.5.

These results show that the Polenske Number is of no value unless carried out under ideal conditions, and that with all the cautions one may use in an ordinary laboratory, results may vary greatly even with the same sample of fat.

From the results obtained from the experimental part of this invesitgation it is concluded that:

1. The Reichert-Meissl Number of butter fat varies from 26.4 - 32.6.
2. The Polenske Number of butter fat varies from 1.55 - 2.7
3. The Reichert-Meissl Number of cocoanut oil varies from 9.5 - 11.3
4. The Polenske Number of cocoanut oil varies from 10.9 - 13.8.
5. In mixtures of butter fat and cocoanut oil the higher the percentage of butter fat the larger the Reichert-Meissl Number and the smaller the Polenske Number, but there is not a definite increase in the one and decrease in the other when definite amounts are used, i.e. when 90 o/o of butter fat and 10 o/o of cocoanut oil are used, the difference between the Reichert-Meissl Number of this mixture and that of pure butter would not be the same as the difference between this mixture and one of 80 o/o butter fat and 20 o/o cocoanut oil. The same is true of the Polenske Number.

6. The following errors may occur in the determination of the Reichert-Meissl Number:
   1-The insoluble acids may hold the soluble ones.
   2-The position of the condenser may cause large quantities of the insoluble acids to collect on the walls.
   3-The method of applying heat may cause the breaking up of other acids.

7. All the errors that may occur in the Reichert-Meissl Number may also affect the Polenske Number and in addition, large quantities of the insoluble acids may collect in the tube connecting the distilling flask and condenser, thus greatly affecting the Polenske Number.

8. The Reichert-Meissl Number checks fairly well in all samples of the fat used, while the Polenske Number varied greatly in the same sample of every fat used, and especially so in the mixtures of butter fat and cocoanut oil.

9. The method used for finding the Polenske Number is not satisfactory because results obtained on the determination of the Polenske Number in the same sample of fat vary greatly.

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