an already peroxidized titanium solution weakens the color. For this reason it is necessary to take the greatest care to insure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the color even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in this country, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the *Technology Quarterly*, **5**, 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralizing with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odor of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which if free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only two or three cc. of the peroxide are employed.

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[FROM THE CHEMICAL LABORATORY OF THE LANDWIRTSCHAFTLICHEN-LANDES-LEHRANSTALDT IN CZERNOWITZ.]

## THE VISCOSIMETRIC EXAMINATION OF BUTTER FOR FOREIGN FATS.

BY DR. NEWMANN WENDER.

Received July 1, 1895.

THROUGH a large number of investigations by Poiseuille, Girard, Hagenbach,[2] Graham, Rellstab, Pribram and Handl, Traube and Gartenmeister, to whose original investigations the reader is referred for the sake of brevity, it has been

[1] *Ann. der Phys. u Chem. Pogg.*, **58**, 424. *Ann. chim. phys.*, **64**, 129.

[2] *Ibid.*, **99**, 217.

established that a relation exists between the chemical composition of liquids and the velocity of transpiration just as there exists a relation between boiling-point and composition. There exists now a criterion for the purity of a substance, if a relation is found to exist between viscosity and boiling-point, at the same time, points of practical importance. From the investigations of Pribram and Handl it follows that observations of the specific viscosity or specific transmissibility of substances afford a hint as to the presence of adulterations and impurities, because these exert a decided influence upon the fluidity. The determination of the viscosity has found a practical value in the examination of oils and beer. The apparatus used for this purpose have been the viscometer of Engler and the septometer, both of which have found extended application. To these valuable, yet always expensive forms of apparatus, I have recently added the "Fluidometer," devised by me and manufactured by the firm of Max Kaehler and Martini, Berlin. I have communicated a description of the same to the Pharmaceutical Society of Berlin.[1] The apparatus possesses besides its inexpensiveness, other merits, chief among which is this, that by means of a simple compression bulb the liquid can be forced back and used for repeated determinations. The apparatus consists of a U formed capillary tube, both of whose limbs are enlarged and divided in such a manner that one arm holds ten cc. and the other two cc. liquid. According to the laws of communicating tubes the liquid flows from the wide limb through the capillary into the smaller limb, which is placed somewhat lower. The viscosity is calculated from the time which is required for the liquid to flow from the first division to the last upper division. There is no danger of error arising from evaporation or contamination with foreign substances in repeating the experiments, and, furthermore, the apparatus is easily and quickly cleaned.

According to the researches of Graham, in 1861,[2] confirmed by those of Pribram and Handl,[3] and by those of Gartenmeister,[4] it was found that the viscosity of a liquid increased with

[1] *Ber. d. Phys. Ges.*, Berlin. *1891*, 342.
[2] *Ann. Chem.* (Liebig), **123**, 90.
[3] *Loc. cit.*
[4] *Ztschr. phys. chem.*, **6**, 524.

the molecular weight, and the correctness of this law is evident from the following table:

| Fatty acids. | Pribram and Handl. Molecular weight. | Specific gravity at 20° C. | Boiling-point. | Specific viscosity at 10° C. | Specific viscosity at 30° C. | Specific viscosity at 50° C. | Gartenmeister. Absolute constant of friction at 20° C. |
|---|---|---|---|---|---|---|---|
| Propionic acid..... | 74 | 0.9929 | 140.7 | 70.3 | 51.5 | 49.9 | —0.1128 |
| Butyric acid ..... | 88 | 0.9580 | 163.0 | 110.2 | 77.4 | 57.6 | —0.1634 |
| Valerianic acid..... | 102 | 0.9386 | 184.0 | 152.4 | 103.3 | 71.5 | —0.2279 |
| Capronic acid..... | 116 | 0.9279 | 199.7 | 222.2 | 139.7 | 97.8 | —0.3263 |
| Heptylic acid ..... | 130 | 0.9163 | 223.0 | .... | .... | .... | —0.4440 |
| Octylic acid..... | 144 | 0.9115 | 237.0 | .... | .... | .... | —0.5860 |
| Nonylic acid..... | 158 | 0.9053 | 253.0 | .... | .... | .... | —0.8480 |

Butter-fat differs from other animal fats in that it contains besides the glycerides of the higher fatty acids, a large amount of the glycerides of butyric, capronic, caprylic, and caprinic acids, and according to the investigations of Duclaux[1] the probable mean composition of butter-fat is:

| | |
|---|---|
| Palmitin, stearin, olein, Traces of myristin butin ..... | 91.5 per cent. |
| Butyrin ..... | 4.2 " |
| Capronin ..... | 2.5 " |
| Caprylin, caprinin, laurin (traces)..... | 1.8 " |
| | 100.0 |

It appears therefore that mangarin consists of the glycerides of palmitic, stearic, and oleic acids only. If we compare the molecular weights of the constituents, it follows that the molecular weights of the glycerides of the higher fatty acids are much higher (806–890) than those of the glycerides in natural butter (302–470). The molecular weight determinations of Gaselli and Carcano[2] showed that the molecular weight of pure butter lies between 696–715 while that of margarin lies between 780–883. The fact that molecular weight stands in close relationship with viscosity was confirmed by Killing,[3] although it is known that

[1] Fleischman, Lehrbuch der Milchwirtschaft, Bremen, *1893*, 30.
[2] Centrbl. Agr. Chem., *1894*, 838.
[3] *Ztschr. Angew. Chem.*, *1894*, 643.

different samples of margarin show variable values, which could appreciably influence the results in the calculations.

Since it has been demonstrated by the work of Traube[1] that the relation between molecular weight and viscosity is not affected by solvents, I used in my "Fluidometer" a solution of the melted fat in chloroform, merely to avoid the difficult operation of maintaining the melting-point temperature of the fat and I did not lose sight of the fact that the viscosity of the solvent had to be taken into account. Chloroform was used, samples of which from different sources, required, in the mean, 20.04 seconds at 20° C. for efflux. The time of transmission of the solvent is set at 100 and the calculations for solutions are based upon this. From a large number of results I present the following average :

| | | |
|---|---|---|
| Viscosity value for pure butter | 344.30 | Time, 68.8 |
| " " " margarin | 373.20 | " 77.4 |

Killings' investigations show further that with the one exception of cacao-fat, whose viscosity value falls below that of pure butter-fat, the values for vegetable fats, used by margarin manufacturers are decidedly higher.

Since, however, mixtures can be made whose values approximate that of butter-fat, the Reichert-Meissl method must be resorted to in order to detect the fraud.

A longer or shorter period of standing of the fat solution does not influence the result, whereas every degree of temperature above 20° C. decreases the time of efflux by 1.45 seconds. On the other hand, a decreasing temperature naturally has a retarding influence which averages 1.43 seconds for every degree. The determination of the exact amount of margarin added to butter when the amount of the former is small, cannot be expected of this method, but a largely adulterated sample is easily detected. From the above the following conclusions may be drawn :

1. The viscosity of butter-fat, in chloroform solution, as well as in the pure state, is always decidedly smaller than that of margarin or its solution of equal amount.

2. While the viscosities of different samples of butter show

[1] Berliner. Ber., *1886*, 871.

relatively small differences, samples of margarin from various sources, show much larger differences.

3. The viscosimetric determination can yield as good service in distinguishing butter-fat from margarin as any other physical method. The amount of margarin added to butter may also be approximately determined.

4. On account of its easy manipulation, its inexpensiveness, and the small amount of fat necessary, the "Fluidometer" is capable of yielding excellent results, not alone in the hands of experienced chemists, but likewise in those of government inspectors, etc.

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## THE EXAMINATION OF LARD FOR IMPURITIES.

By David Wesson.

Received June 22, 1895.

IN examining a sample of any material for impurities the analyst must first familiarize himself with the pure substance before he can detect wherein the sample under examination differs. If a definite compound is being dealt with, the problem is an easy one, but if we have an organic substance, which from the very nature of its origin is subject to many variations, the analyst is confronted with a problem of no small magnitude, and this is very true in regard to the accurate analysis of commercial lard, which is the fat rendered from various parts of the freshly slaughtered swine. Hogs being omniverous animals, it is reasonable to suppose that the fat will vary in accordance with the feed. It is a well-known fact that the lard from hogs which have been allowed to run in the woods and fatten on nuts of various sorts, preserves in a marked degree certain properties of the nut oils, and is much softer, containing more oil than that made from corn-fed hogs. That animals under proper conditions absorb food directly and deposit the same more or less unaltered in their tissues, seems to have been proven by experiments made some years ago at the Munich Physiological Institute.

That the fat varies greatly in different parts of the same animal has been demonstrated by various observers[1] as well as the writer.

[1] Wiley: Bulletin 13, Part IV, U. S. Dept. of Agr.; R. T. Thomson and H. Ballantyne; *J. Soc. Chem. Ind.* 9, 589, (590).