5. Another item to be considered in studying shelf storage is the state of fullness of a sealed package. There are reliable data which show that a package half-filled with fat develops rancidity in a shorter time than does fat in a package which is full (18).
6. The presence or absence of oxygen in the package is of importance. An inert atmosphere will cause higher stability figures to be obtained than if the atmosphere overlying the fat is oxygen or contains oxygen.

The amount of air whipped into the fat is also of importance. It is common in commercial practice to include air or an inert gas in the fat as a means of obtaining a lighter product. This air is intimately mixed with the fat molecules, and it is quite reasonable to suppose that it will influence the stability data obtained.

It is assumed in all the discussion in this paper that the technician is practicing meticulous cleanliness of all materials which come in contact with the fat during testing. In the absence of extreme cleanliness it is useless to apply any test at all.

A DISCUSSION of this type should include mention of a problem which is particularly important in the current studies on the evaluation of antioxidants in the stabilization of edible fats. Even though, by some of the methods described here, it is possible to determine the stability of a fat in question, the stability data so obtained cannot be applied to the food products made from the fat. It has been the experience of a number of people working on antioxidants that, while a fat may be stabilized to a very high degree as judged by accelerated methods of testing, the food products prepared from this fat may have a stability only slightly greater than that of food prepared from the unstabilized fat. Here again we are faced with the problem of determining the stability in such a manner that the data will be useful regarding the final product which we intend to use.

Our method of determining the stability of pastry is to place a number of broken pieces of the product in 4-oz. mayonnaise jars with screw tops and store them at room temperature or in the Schaal oven in the absence of light. At regular intervals, samples are removed, tested for peroxide content, and examined for organoleptic indications of rancidity. It is usually found that the stability data as obtained on the fat before its use in cooking is of very little value in predicting the stability of the pastry or other food material prepared from the fat in question.

In summary, it should be stated that just as there is no completely reliable chemical test for rancidity, there is no completely reliable laboratory test for stability. Rancidity is ultimately determined by taste and smell, and stability is ultimately determined by placing the fat in storage and allowing it to become rancid. Even then, the food products prepared from the fat may not possess a stability even remotely like that of the fat from which they were prepared. In spite of these inadequacies in our laboratory methods, however, much valuable time is saved through accelerated tests, and much information is obtained which serves as a guide for planning a relatively small number of well-chosen experiments on an elaborate scale for the final investigations. This was especially true during the war-time emergency when we needed to use these rapid tests for evaluating materials for their antioxidant effectiveness.

By means of the accelerated tests described and with full knowledge of their limitations the chemist is making rapid progress in food stabilization.

REFERENCES

1. Burr, G. O., and Barnes, R. H. Physiol. Reviews *23*, 256-278 (1943).
2. Fridericia, L. S. J. Biol. Chem. *62*, 471-485 (1924).
3. Cummings, M. J., and Mattill, H. A. J. Nutrition *3*, 421-432 (1931).
4. Norris, L. C., Heuser, G. F., and Wilgus, H. S. Mem. Cornell Agr. Exp. Sta. No. 126, 3-15 (1929).
5. Lea, C. H. Rancidity in Edible Fats. Food Investigation Special Report No. 46, London.
6. Lea, C. H. Proc. Royal Soc. (London) B108, 175-89 (1931).
7. Pool, W. O., Oil and Fat Industries *8*, 331-336 (1931).
8. King, A. E., Roschen, H. L., and Irwin, W. H. Oil & Soap *10*, 105-109 (1933).
9. Blank, E. W., Colt, E. W., Dollear, F. G., Laing, M. J. L., Fitelson, J., Long, C. P., Maroney, J. E., Milner, R. T., Parsons, L. B., Schuette, H. A., Sorensen, S. O., Tolman, L. M., Woekel, F. C., Mehlenbacher, V. C. Ind. Eng. Chem., Anal. Ed. *17*, 336-340 (1945).
10. Jany, J. Z. angew. Chem. *44*, 348 (1931).
11. Johnston, W. R., and Frey, C. N. Ind. Eng. Chem., Anal. Ed. *13*, 479-81 (1941).
12. Nagy, J. J., Vibrans, F. C., and Kraybill, H. R. Oil & Soap *21*, 349-352 (1944).
13. Nagy, J. J., Beadle, B. W., and Kraybill, H. R. Oil & Soap *22*, 123-4 (1945).
14. Kreis, H. Chem. Zeit. *26*, 897 (1902).
15. Barnicoat, C. R. J. Soc. Chem. Ind., Lond. *50*, 361T (1931).
16. Coe, M. R., and LeClerc, J. A. Oil & Soap *12*, 231-233 (1935).
17. Greenbank, G. R., and Holm, G. E. Ind. Eng. Chem. *33*, 1058-60 (1941).
18. Clarenburg, A. Tijdschr. Diergeneeskunde *68*, 192-7 (1941).

Methods of Sampling Bulk Oil With Particular Reference to Bleeder Samples

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THE subject of bleeder samples arises more often in connection with bulk oil shipments than with tank cars or land storage tanks and requires special thought when intended for ship's tank deliveries. When considering the results of this method in comparison with core samples taken by other recognized means, such as the sectional zone sampler or thief in illustration, numerous factors must be taken into account and understood before correct conclusions can be reached.

First and foremost, however, it should be emphasized that nothing can take the place of sound judgment and technical understanding in the use of these devices and methods based on wide and diversified experience in this field (5). Knowing when and how to apply particular methods or equipment and when their limitations make their use inadequate is a fundamental necessity in the science of sampling if dependable results are to be expected. Applying any recognized method of sampling in itself does not assure accuracy in all cases; it is the character of the equipment, its appropriate application to the particular circumstances involved and the ability to secure mathematical proportions representing all parts alike that regulate the outcome. No sampling device, however orthodox, can automatically correct the many divergent conditions that may arise, nor is there any "rule of thumb" procedure which in itself is adequate under any or all circumstances.

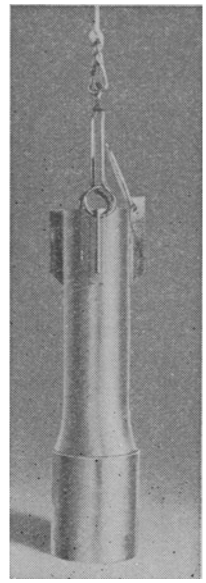
The bleeder is a representative method of sampling if understandingly used and properly installed and watched, but as was pointed out in the writer's report to the American Oil Chemists' Society Sampling Committee (4) this is rarely the case. The usual equipment is a small valve or petcock and bleeder pipe placed on the underside of a horizontal supply or pump line with the intention of collecting a small uniform flow of oil during the entire period of loading or discharge. However, this type of installation is frequently unreliable for the following reasons:

Any free water or heavy emulsion tends to gravitate more or less towards the bottom of the line and may be represented in a greater proportion than truly exists. This can produce unrepresentative results in just the same manner as the geometric error does when taking a core sample from a settled tank car.

Another disadvantage in this method is that meal, or other suspended matter usually present in crude oils, tends to clog the valve, causing the flow to lessen gradually and sometimes stop altogether, thereby preventing a uniform representation being procured during the entire pumping period. This difficulty is partially overcome by opening the valve sufficiently to clear the bleeder of its obstruction, but after that the flow is seldom restored to its original rate and this change causes another variation, besides the possibility of the stoppage re-occurring.

If the tap is turned on more fully in the beginning to lessen the possibility of such clogging, then an unwieldy amount of sample is obtained that requires numerous containers to be watched and changed and later blended and resampled.

THE bleeder installation is of necessity on the pressure side of the pump and theoretically responds proportionately to variations in line pressure. The pressure on the line is regulated by the rate of pumping and by the line friction and height or head to be overcome. The latter naturally exerts a back pressure in the line which is present even when the pump is not running, and if pumping is interrupted at any time, as is frequently the case, and the bleeder is not shut off, the sample will continue to receive oil from the line, a circumstance which again produces disproportionate results. Further, near the end of discharge and during the cleanup when the pump is not always working at full capacity, the bleeder will continue to deliver a disproportionate amount of oil due to the back pressure, and the oil at this time is generally the highest in moisture and insolubles. Frequently when bulk shipments are pumped to storage tanks, the oil is delivered to the storage tank through an overshot, that is, to the top of the tank, which results in a uniform back pressure. If, however, the oil is pumped into the bottom of the tank, the back pressure gradually increases due to the increasing head and is greatest at the end of discharge during the critical period when the poorest oil is being pumped, which introduces still another variable to be considered.



Curtis and Tompkins Zone Type Oil Sampler.

Most frequently the bleeder is left for long periods without attention and during that time may clog and run at a gradually diminishing rate or even stop for a considerable period without notice. These differences or lack of flow might well occur during a critical time in the discharge which would have a marked effect on the character of the sample that is supposed to represent the shipment as a whole. While the popular impression that the bleeder once set requires little attention may hold with clear oils free from settlings, such as water, emulsion or insoluble matter, and stearine, it certainly does not hold for crude oils where these ingredients may be present to a greater or lesser extent and when variable back line pressures occur during pumping interruptions.

In addition to the foregoing main sources of error in bleeder samples there are several others. For example, often two pumps of different and varying capacities are used on the same shipment, each discharging through a separate line to the same storage tank. Even though an adequate and exact bleeder sample were taken from each line, there would be no way of knowing in what ratio to blend the two portions. Again there is the effect of a booster pump in an extremely long discharge line. However, to cover completely all contingencies would extend this article beyond its intended limits. Unusual problems, as previously pointed out, should be dealt with as such by adequately trained personnel employing technical knowledge, not just instruments and rules.

With normal shipments, the core sample taken with proper zone or plunger type equipment is equally, if not more representative than a sample taken with the usual type of bleeder installation. If, however, there is water at the bottom of the ship's tank, a list to one side or the other may cause the water to concentrate at a point in the tank where the sampler does not reach or pile it up on the side where the plunger would take a greater proportion than truly exists. Under these conditions, therefore, there is a better opportunity of procuring a representative sample with the bleeder though even with frequent inspection to maintain a steady flow throughout the pumping period, the amount of water indicated is generally exaggerated for reasons already mentioned.

However, the zone sampler usually reveals the presence of extraneous water in advance because a bottom sample can be taken independently of any other part of the tank and the presence of free water is indicated by some emulsion if not by the free water itself. In such cases, in order to obtain a representative sample of the whole shipment individual tank car samples are drawn immediately after cars are filled when the oil is in a thorough state of admixture, and parts of these samples are composited for analysis. When a shipment of this nature goes directly to storage, a core sample is taken from the land tank immediately after discharge when the oil is still mixed and before settling takes place. Either of these methods, or a combination of the two (tank car and storage tank sampling), produces better samples than generally are obtained by other means and certainly better than the usual horizontal line, seldom attended, bleeder type installation.

ANOTHER factor not always recognized is that the composite average sample procured from the ship's tank either by the plunger (thief) or bleeder method does not necessarily represent the individual composition of any one car. If tank cars are filled from a shipment containing excess water, meal, etc., at the bottom of the ship's tank and pumping starts well off the bottom or near the top, as is usually the case, the oil going to the first tank cars is naturally the best oil while the last cars filled from the lower or bottom portions of such ship's tank receive the major portion of the water and meal. If on the other hand the ship's equipment is used to discharge the oil, the pumping is from the bottom of the tank and while the settled material may then be transferred to more cars, the first cars filled receive most of it and the last cars pumped will contain the best oil (least settled material), except for the final "rub out." Therefore individual car samples are a necessity unless the entire shipment is delivered as a unit since the composition of the entire ship's tank may be one thing and the individual tank cars quite another as far as the amount of moisture and insoluble impurities are concerned.

If there were any means by which the oil in ship's tank could be thoroughly mixed so that all the settlings at the bottom could be completely and uniformly distributed throughout the entire shipment and kept so during the entire pumping period, then every car filled from such a tank would be alike in composition and the sample from any one car would be the same as any other and the ship's tank sample would be just as representative as any of the tank car samples. As such ideal conditions are unattainable, the situation must be dealt with practically by using whatever means are available to obtain the best protection, which obviously requires sampling each individual tank car from which a composite is made or sampling the land tank immediately after discharge is completed (or both in the case of split shipments) in addition to sampling the ship's tank.

Throughout the foregoing we have been referring to the variables such as water and insoluble matter, not to the actual character of the oil itself, free from materials capable of settling and changing in quantitative relation to the rest of the oil. The composition or purity of the clear oil does not change in that way, nor does it alter from one car to another. Any variation in the oil proper that may have existed when first loaded into the ship's tank has long since been overcome by constant agitation and mixing during transit, and a sample from the top or bottom of ship's tank or any tank car would give practically the same analysis except for moisture, meal, foots, or stearine. The oil incorporated in the settling zone at the bottom of the land storage tanks does increase in free fatty acids to a greater or less extent depending on environment and the nature of the oil, but with oil shipments constantly in motion this is a negligible factor.

When confronted by a large excess of water in ship's tank due to leakage or other causes, the normal procedures outlined above for procuring average samples become useless. In such an event, the bottom oil and emulsion are usually handled separately and pumped into a separate container for reconditioning, leaving as much free water as possible in ship's tank for further consideration. Sometimes reconditioning requires the application of heat or other methods to break the water emulsion while in other cases free water will settle out after standing. In any event, when as much water as possible has been separated and drawn off, moisture is determined in the remaining oil and the weight corrected for anything in excess of the normal amount in the undamaged portion of the delivery or as determined on the basis of the shipping sample.

The experience gained from many past shipments clearly demonstrates the latitude needed in handling individual cases as they arise if a true and average representation of the ship's tank or tanks as a whole is to be secured and also shows that the ordinary bleeder as usually installed does not always produce representative samples as a basis of settlement.

A properly installed bleeder should be set at some point on an upright portion of the feed pipe or supply line where there is less tendency to procure disproportionate amounts of water, etc., than when placed on a horizontal line. One of the more desirable types of bleeder has four ½-inch openings at equal spaces around the supply line and each connected by piping (without valves) to a 1-inch main bleeder pipe fitted with control valve or faucet to regulate the flow. As a precaution, this bleeder section should be set in the supply line with unions to facilitate removal should cleaning become necessary. Like all bleeder type installations, however, it must be carefully watched and regulated. The sample is collected in a suitable container and thoroughly mixed and subdivided at completion of pumping. Reference to two other bleeder types developed to help overcome the defects of the single pipe and petcock will be found in the writer's report to the Sampling Committee (4).

REFERENCES

1. "Report to Committee on Sampling and Testing Copra," The Cotton Oil Press, July, 1920.

2. "Errors in Official Method of Sampling Tank Cars," The Cotton Oil Press, Jan., 1921.

3. "Sampling Coconut Oil in Tank Cars," The Cotton Oil Press, June, 1921.

4. "Samplers and Sampling of Vegetable Oils," The Cotton Oil Press, Dec., 1921.

5. "Notes on Sampling Deep Sea Tanks," The Cotton Oil Press, Feb., 1922.

6. "Sampling Committee Report," The Cotton Oil Press, June, 1923.

7. "Copra Sampling and Inspection," Oil and Fat Industries, Jan., 1927.

8. "Copra Quality Under New Rules—Importance of Sampling and Analysis," Oil and Soap, May, 1941.