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Sampling

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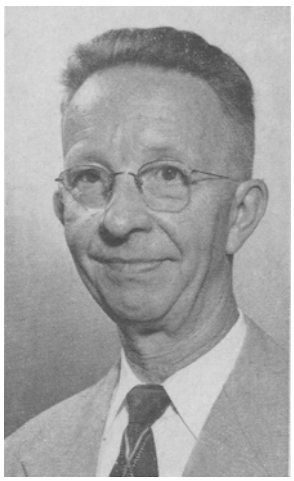
THE MATTER of sampling is of extreme importance, and as so often has been stated, "an analysis can be no better than the sample on which it is made." In this discussion few details of various sampling procedures will be described since methods books and rules of the various technical and trading associations cover these procedures in considerable detail. We shall therefore confine ourselves for the most part to the general aspect of sampling various sorts of materials, realizing that perhaps all of you are interested not only in fats and oils but in other commodities as well.



L. R. Brown

General History of Sampling

The word "sample" is based on the Old French "essample" (example) and the Latin "exemplum," and therefore means "example." According to Webster's definition, a sample is "a specimen; a part of the whole taken or presented for inspection as evidence of the quality of the whole." This definition leads us to believe that the terms "sample" and "sampling" are quite widely misused because it should be noted that a sample represents the entire lot of the commodity under examination. In a great many textbooks on analytical methods the instructions begin with the statement, "take a representative sample . . . ." It would appear that the term representative is superfluous since by definition a sample in the truest sense of the word should represent the entire lot of the material being checked. The display of samples to represent merchandise or commodities of any sort is as old as commerce or trade and has always been the means by which articles of all sorts are offered for sale or barter. Evidences of this even go back to Biblical times, and certainly the display of samples of merchandise is the order of the day in our time. The use of transparent packages whether they be glass, plastic, cellophane, etc., is in such common use today that most of us expect to be able to see what we are buying, and certainly reports covering retail sales bring out the justification for this system of merchandising.

This perhaps seems a far cry from sampling a tank car of crude soybean oil, but the point I wish to make is that in both instances attempts are being made to display or obtain a sample of the material being dealt with. In the case of the farmer, the grain he will buy or sell is sampled, and if he is putting in a crop of corn, for example, he will have the seed corn sampled and a germination test made prior to

planting. During the growing season the development of the crop will be judged by sampling the field in one way or another, and in most cases by the time the crop matures, he will have a fair estimate as to what the yield and quality of his corn will be. In grain trading circles sampling serves as a basis for all quality characteristics determined in the grain and therefore has a direct bearing on the trading price of the commodity. Specific instructions regarding sampling techniques are covered in the Federal Grain Inspectors' Manual, and in every case proper sampling procedures are certified to by the inspector. Most processors of cereal grains and other oil-bearing seeds sample their receipts and, upon these samples and the analyses made on them, base the efficiency of their processing operations.

Perhaps the handling and preparation of samples submitted to the laboratory should also be considered in a discussion on the sampling problem. Samples submitted for analysis are usually presumed to be well mixed, but our experience has shown that this is not necessarily always true. One of the first duties of an analyst therefore should be to make certain that the sample which he is examining has been thoroughly mixed and is uniform throughout, and that the portion he removes for analysis is a thoroughly representative portion, or a true sample, of the material on which the analysis is to be made. This, of course, is particularly true in the case of dry materials having appreciable variations in particle size, or in the case of liquids where there is danger of settling or stratification.

Another very important aspect of sampling is to be found in the control of processing operations in almost any industry, and in these instances attempts are made to obtain representative samples from various key points in the process. It is of course not always possible to obtain continuous or flow samples throughout an entire process, but attempts are always made to sample these points at regular intervals and in a uniform manner. The data from these samples serve as a guide to the operator on this particular phase of the work. In our own particular case where we process both corn and soybeans and their derivatives, samples run into the thousands per day, and proper sampling with us is considered to be extremely important and a never-ending problem. We are quite certain that this same condition applies to all other processing industries, regardless of the type of work being done.

Development of Sampling Methods

It is quite probable that in the early days dip samples were taken, probably with a hollowed-out gourd or some sort of an earthenware vessel with no attempt to get a representative portion of the material being sampled, and probably with no mixing or agitation to insure uniformity throughout the body of the material. Later probably some sort of a bottle or dipping arrangement was resorted to and possibly the so-called top, center, and bottom sections were sampled. This procedure was improved somewhat by the development of the oil thief, a cylindrical device with a valve in the bottom which could be opened and closed at specified sampling levels. From experience I know that this procedure was used a number of years ago in crude petroleum production where gaugers would sample storage tanks and submit the samples to the laboratory for the determination of water and bottom settlings, which was a water-oil emulsion. Later developments probably led to the taking of intermittent flow samples, and ultimately to bleeder or continuous flow samples of one sort or another. Today there are innumerable types of sampling devices, all designed to improve sampling techniques in industry and trade. These devices include such equipment as core samplers, bomb or zone samplers, triers, oil thieves, bleeder or petcock installations, etc. Examples of a few of these pieces of equipment are as follows:

For Dry Materials	*For Liquids and Semi-Solids*
6-in. Bag Sampler	Core Sampler 2 in. x *ca.* 10 ft. (tank cars)
18-in. Slotted Bag Trier	Core Sampler 2 in. x 3 ft. (drums)
18-in. Open Trough Bag Trier	Bacon Bomb Sampler
Grain Sampler	Trier for Solid Fats ½ in.–1 in. x 2 ft.–7 ft.
	Tank-O-Scope

In the most recent revision of the A.O.C.S. Book of Methods 28 pages are devoted to sampling procedures of the materials covered by this book, and 16 pages describe sampling procedures for oils, fats, and related products. It is quite obvious that, in devoting this much space to sampling procedures and techniques, our Society recognizes the extreme importance of this phase of the work and takes every precaution to insure accuracy and uniformity throughout the entire process of obtaining, handling, and preparing samples. Other technical and trade

Index

associations also have their sampling procedures, and to mention a few of these I might cite such organizations as A.O.A.C., N.S.P.A., N.C.P.A., A.S.T.M., and A.A.C.C. Obviously time does not permit a detailed discussion of these various procedures, but in all cases sampling rules laid down by these organizations represent their best attempts to regulate sampling procedures so that samples obtained as directed will be true or representative portions of the commodity being examined.

At the present time the A.O.C.S. is attempting to develop a continuous-flow sampling procedure for tank cars of oil that will replace the present petcock procedure given in Method Cl-47. The procedure, when and if developed and approved, will undoubtedly be applicable during loading or unloading of the car. Such a procedure has not yet been adopted by the Society, but we feel confident that some method of this type will ultimately be approved. In this connection it might be mentioned that extreme care must be taken in sampling crude oils since many of them contain sediment or settlings. This extraneous matter tends to plug the petcock and virtually serves as a strainer, thus clarifying the oil as it flows through the petcock to the sample container. We know of two interesting occurrences which illustrate this point. A soybean processor had several plants and, as is customary in situations of this sort, the quality of the oils produced from the several plants was observed regularly and each oil was compared with the others. It was learned that one plant consistently seemed to be producing practically clarified oil while the other plants were putting out a normal quality of crude soybean oil, and, as might be expected, management inquired why their oil quality was inferior to that of the other plant. Investigation revealed the fact that the plant producing the superior oil was using a petcock sampling procedure, and although they had been given credit for a better grade of oil, it was soon learned that improper sampling accounted for the apparent superiority of the product. In another case, also of a soybean processor, difficulties were encountered between buyer and seller. The seller's sample taken at the time of loading was a nice clear oil, completely free of sediment or settlings, while the buyer was reporting the oil to contain the normal amount of sediment, phosphatides, etc. The seller's sample was being taken by a petcock procedure while the buyer's sample was being obtained with the official core sampler taken from the car upon arrival. Needless to say, both of these conditions were changed. In the trading of crude soybean oil, price is adjusted on the basis of the standard laboratory refining loss, the premium or penalty being 3/4 of 1% of the contract price for each 1% below or above 7%. Assume that, due to improper sampling, seller's and buyer's analyses disagreed by 2.0%–5.0% against 7.0% and that the contract price was 12 cents per pound. On a standard 60,000-lb. delivery, there would be a price difference of $108.00 as calculated from the two sets of results, and such a discrepancy would be intolerable to both parties in the transaction. Such differences as this are not unusual and are generally traceable to sampling rather than to analytical causes.

Sampling Problems to Be Overcome

In the case of storage tanks, tank cars, drums, barrels, etc., which have been freshly filled, or in which no settling or sedimentation has occurred, regular core, bomb or zone, or thief sampling procedures are probably satisfactory, but such is not the case where the contents of the container do not run uniform throughout the body of the oil. In this connection under A.O.C.S. Official Method Cl-47, Paragraph C, the following is noted:

1. It is impossible to write directions for sampling fats and oils that will encompass all conditions and circumstances that may confront the individual charged with the responsibility of taking the sample. There are many instances in which the experience and judgment of that individual must prevail. There are however certain general rules which must always govern if the sample is to be representative.
2. The best sample of bulk oil quantities can be taken if the product to be sampled is completely liquid and thoroughly mixed. In such cases a core sample or even a sample dipped from the tank while undergoing vigorous agitation will be representative.
3. Settled material in which the water and solid impurities are likely to be concentrated at the bottom is difficult to sample and reconstitute in proportional quantities. The contour of the tank must be taken into account. If the bottom of the tank is smaller than the middle or top, or *vice versa*, a core sample is not adequate. To overcome this the number of portions from each section (*e.g.*, each 1-ft. level) should be regulated in reverse order to the cubical capacity of each section. For example, if the bottom 1-ft. section is one-fourth of the middle 1-ft. section, then one 1-ft. sectional sample should be drawn from the bottom level and four 1-ft. sectional samples from the middle section. These portions are then composited into one sample and mixed.

Actually it would seem that in practically all cases such a procedure as this should be followed in sampling tank cars because one can never be certain that the oil is uniform throughout the load. In the case of sampling packages of any product whether they be drums, barrels, bags, etc., practically all sampling regulations call for a minimum of 10% of the packages to be sampled, and, of course, specific instructions are given as to how the samples are to be drawn. I know of a recent case in which a car of sacked soybean meal showed a moisture content of slightly over 14%, and a check determination confirmed this value. A re-sample was taken from the car and showed only 12%, and a second re-sample was resorted to. This latter sample, having been taken properly, checked the original result of 14%. It was found that, in the case showing only 12% moisture, the sample had been taken from only a few bags from the load and that a bag sampler not over 3 in. in length had been used. A difference of this magnitude would be the equivalent of 1,600 lbs. of meal in an 80,000-lb. load and would certainly give rise to trouble between buyer and seller. Certainly an occurrence such as this points up the necessity for proper sampling techniques and illustrates what can happen when incorrect procedures are used. In a recent private communication from a friend of mine having to do with the subject of sampling he stated: "frankly I believe that the sampling problem is mainly an educational one. No one should be left with the opinion that the sampling operation is a water-boy job."

In looking over some literature on sampling, I ran across an article by Tompkins and McElligott in the Cotton Oil Press of 1920. The following statement, which is probably just as true today as it was then, read: "while the majority of disputes arise from defective sampling, the average person engaged in business requiring this service does not fully appreciate its significance. Most contentions follow on the assumed inaccuracy of the analysis whereas in almost every instance it is directly traceable to the

manner of procuring and preparing the sample, and it should therefore be the policy of those best informed to bring its needs clearly before parties concerned as a means of eliminating disputes and as a basis of correcting errors." Any of those present who have had experience in buying or selling crude soybean oil, where price is based on refining loss, will appreciate the significance of this statement, particularly in view of the example. In this connection we have found that the use of a divider or riffle is quite effective in reducing the gross sample taken from a car of soybean oil to the required three 1-gal. samples specified in trading rules.

Conclusion

It is hoped that the foregoing general remarks on sampling procedures will point up the necessity for more care in this very important operation. In too many instances sampling has been delegated to persons not too well aware of the purpose and importance of the samples which they are taking, and possibly not too well qualified to handle the job. This situation could be improved markedly by better training and instruction of persons delegated to take samples, or preferably by selecting persons better qualified and more interested in this essential but rather non-glamorous operation. There is also the need for better equipment specifically designed to handle the more difficult and troublesome sampling situations, some of which have been mentioned previously. Much unnecessary work on the part of the analyst could be eliminated, and at the same time his prestige could be raised materially, if the samples he received for analysis were always true and representative parts or segments of the entire lot of material on which his evaluation is based.

Determination of Impurities in Fats and Oils

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IMPURITIES present in fats and oils and fatty acid products are mainly moisture, volatile compounds, insoluble matter, unsaponifiable matter, trace metals and their soaps. The term M.I.U. (moisture, insoluble, unsaponifiable) is a frequently used group designation for the determination of the non-fatty constituents of crude oils and other fatty acid products where settlement is on the basis of oil or acid content. It also figures predominantly in the trading rules of the various oil trading organizations, such as the National Soybean Processors Association, National Cottonseed Products Association, New York Produce Exchange, and the National Institute of Oilseed Products.

A. A. Rodeghier

Moisture and Its Determination

Moisture is such a universal constituent of all materials analyzed in the laboratory that its determination is probably the most common of all those conducted.

One of the most common methods of determining moisture in a fat or oil is that by the "hot plate" method (1). In this method approximately 10 g. of a representative sample of the oil is weighed into a clean, dried tared beaker. This is then heated on a hot plate, applying gentle rotation by hand. As the end-point is approached, the absence of foaming and steam vapor is apparent, and heating is continued until incipient smoking of the sample occurs. The beaker is then cooled in a desiccator and weighed; percentage loss is calculated as moisture and volatile matter.

The "oven" method (2) is more time-consuming than the "hot plate" method, but results are more accurate and reliable. This is even more true when using the vacuum oven. In the "oven" method for moisture a representative sample of approximately 5 g. of the oil is weighed into a dried, tared moisture dish. It is then set into the oven for 30 min. at 101 ± 1°C., cooled in a desiccator, and weighed. Continued heatings and weighings are necessary to obtain a constant weight. Loss in weight is again calculated as moisture and volatile matter.

A forced draft oven reduces the drying time by the sweeping away of the moisture molecules by diluting the vapor with warm air so that more of the water molecules can escape from the liquid phase. Drying is usually about four times faster in this type of mechanical convection oven than in a gravity convection oven. A forced draft oven also tends to maintain a more uniform temperature throughout the oven drying chamber.

The "vacuum" oven method (3) is applicable to all fats and oils and for various other materials where moisture is deep-seated and must diffuse largely through the capillaries. A decided advantage may be gained by using the vacuum oven. The same technique is followed for the oven method except that the sample is dried in a vacuum not exceeding 100 mm. of mercury at a temperature not less than 20°C. and not more than 25°C. above the boiling point of water at the operating pressure.

Today there are various kinds of moisture testers available for the determination of moisture in all kinds of materials. One device measures moisture content on a modified conductivity principle where no sample weighings are required and results are obtained on a calibrated dial. Another rapid drying moisture teller uses a stream of air at a controlled temperature and velocity to flow over or through the sample, giving results in a few minutes. Another unique method for determining moisture is one called a "moisture balance." This apparatus has a built-in torsion balance, the sample is placed on the pan, and infrared heat is applied until all the moisture is driven off. The percentage of moisture is read directly from a dial scale.

The "distillation" method (4) for moisture is