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and **J.B. Rossell**

Analysis of
Oils
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ANALYSIS OF OILS AND FATS

Edited by

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FOREWORD

The Federation is representative of producers, dealers, brokers, oilseed crushers, refiners of oils and fats—indeed of all those involved in the international trade in these commodities. It issues contracts to ensure the smooth flow of these commodities from the producing country to the end consumer. All the contracts for oils and fats include quality specifications which have to be determined by analytical methods. Most, if not all, of the contracts require that the oil or fat shall be of 'good merchantable quality'. This is something which is very hard to define but, in assessing it, analytical work will be required.

All the methods described in this work by Dr Hamilton and Dr Rossell are of relevance in one way or another to the determination of quality specifications or as an aid in determining whether an oil or fat is of 'good merchantable quality'. It will therefore be of interest not only to the scientific community which serves the trade but also to those who produce the raw material, those who trade it on the international markets, those who buy it in consuming countries and those who refine it.

It is an erudite work which brings together, inside one cover, probably all the most important references to the analysis methods applicable to oils and fats. It is to be highly recommended both to scientists and to those in the international trade.

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Chapter 1

CLASSICAL ANALYSIS OF OILS AND FATS

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1.1 INTRODUCTION

In contrast to the other chapters in this book, this one will deal with the traditional or classical methods of analysis. By and large these may be called 'wet chemical tests', although a fair proportion, such as measurement of colour, or determination of flash, smoke or fire points do not involve any liquid titrant, solvent, or bath. The factor that the tests do have in common is that they are used extensively to assess the commercial quality or value of an oil. In the author's view, 'classical' tests are used much more extensively than the more modern instrumental methods of analysis for these commercial value assessments. It may be held that this is because the significance of 'classical' tests has had longer to penetrate the commercial world, but it is far more likely to be because they have an intrinsic merit, and that the tests were devised of necessity in time past in order to measure the truly important properties of an oil.

Modern instrumental tests may give more information, but is it on a scale of diminishing returns? The free fatty acid content of an oil is a very good guide to the relative proportions of neutral and acid oils that will be produced during the refining process. This has a real commercial significance outweighing by far the value of a differential thermal analysis (DTA) or nuclear magnetic resonance (NMR) result on the oil. The classical tests should never therefore be regarded as unimportant. Less glamorous or less sophisticated they may be, but they are collectively the most important measurements of an oil's quality.

Another factor in comparing 'classical' tests to others discussed in this book, is that the theoretical background to many of them may be more difficult to understand. Although the experimental procedures have been evolved over a number of years, the chemistry is not always understood in full. What is the basic reaction in the thiobarbituric acid (TBA) test for instance, and what is the nature of the chromogen produced? Do any side reactions influence the measurement of iodine value? To what extent does a variation in human eyesight, from one observer to the next, influence the measurement of Lovibond colour, and how can this best be alleviated? How much easier to follow the mathematical theory of some of the modern approaches to analysis, such as the various forms of spectroscopy.

As the basic chemistry is not always straightforward the 'classical' tests are often empirical, or have empirical steps in them. In these cases slight variations in the experimental procedure can cause a variation in the experimental result. This is especially the case if any 'shortcuts' are taken. Any such variation in the results can of course have important consequences, especially when the commercial value of an oil or fat is dependent on the accuracy of the analytical result. For these reasons the majority of the 'classical' methods discussed in this chapter have been standardised in such a way that the scope for operator error has been reduced to an absolute minimum. The reliability of many of the experimental procedures has been established by collaborative ring tests, or with some of the older procedures by years of experience and consultation between laboratories throughout the trading world. The methods have thus become optimised, and are now available in the form of standard tests such as those published by the British Standards Institution (BSI), International Organisation for Standardisation (ISO), International Union of Pure and Applied Chemistry (IUPAC), the American Oil Chemists' Society (AOCS), the Association of Official Analytical Chemists (AOAC), the Deutsche Gesellschaft für Fettwissenschaft (DGF), etc. A cynic may say that there are too many standardisation bodies, with the result that there are a plethora of methods rather than a uniformly accepted standard procedure. While there may be some truth in this view with some tests, by and large these different bodies have published methods which are often identical in all but minor details. Nevertheless, it is often wise to check which standard method (or local variation?) was used in each of the laboratories, when otherwise inexplicable variations in results come to light.

The problems of experimental error and validity of the analytical result do of course depend on several factors. These include the error inherent in the analytical method itself, experimental error introduced by the analyst (however skilled), and sampling error. The uniform and standard methods published by the aforementioned bodies have been developed with the objective of keeping the first two of these sources of error to a minimum, but they can do nothing to alleviate errors caused by sampling procedures. The first section of this chapter therefore deals with the problems of sampling in its various forms. Subsequent sections then deal with basic quality control tests, analyses used in the assessment of oil purity, methods for the determination of trace impurities and contaminants, and finally the measurement of physical properties.

1.2 SAMPLING

The errors involved in sampling are often overlooked. They fall into two types: the first being the actual taking of the sample, whilst the second is the reduction of the sample received in the laboratory to a condition suitable for analysis. The former of these may involve sampling a ship's tank, a pile of drums, or an oil stream in a factory process. In many cases the laboratory analyst is unable to influence the course taken, but it is best that he be acquainted with the facts relevant to the manner of sampling used. Almost all oils and fats are sold on the basis of a sample, which is then analysed in the laboratory, and disputes are usually resolved by reference to a sample. Careless or inaccurate sampling can therefore lead to misunderstanding, delay, or unwarranted financial adjustments.

The International Organisation for Standardisation has therefore developed the International Standard ISO-5555—Animal and Vegetable Fats and Oils—Sampling. This is largely based on the British Standard BS 627 (1982), which covers sampling technique, methods of sampling, packaging and labelling of samples, the despatch of samples and the preparation of a sampling report. Various types of apparatus are needed for adequate sample taking, depending upon the nature of the fat or oil to be sampled. Several typical examples of sampling apparatus are shown in Figs 1.1–1.4.

Figure 1.1 shows a sampling bottle or can, suitable for sampling

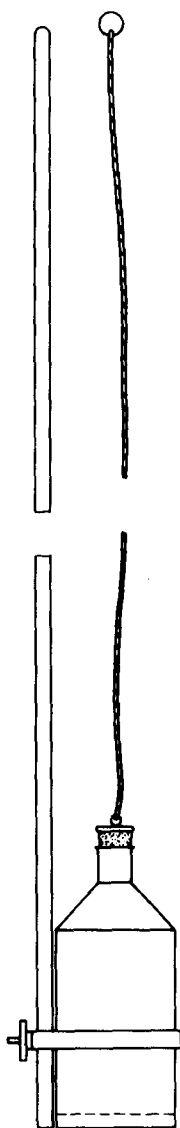


FIG. 1.1. Sampling bottle. (Reproduced with permission of the BSI, London.)

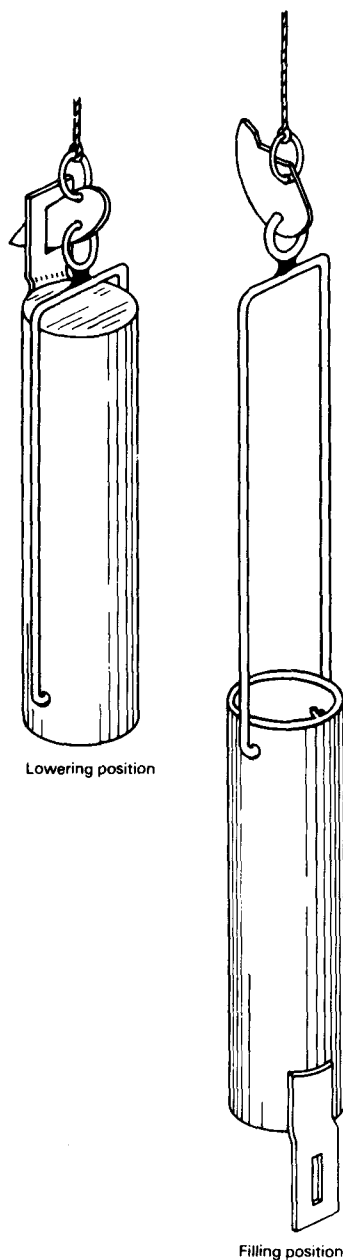


FIG. 1.2. Sampling tipping dipper. (Reproduced with permission of the BSI, London.)

large vessels or tanks of liquid oil. It consists of an optionally weighted container attached to a handle long enough to reach to the lowest part of the tank. It is equipped with a removal stopper which can be removed by a 'tug' on the chain or cord. The device is lowered to the desired depth, where the stopper is removed, allowing the container to fill.

A sampling tipping dipper is shown in Fig. 1.2. This consists of a cylinder of about 150 mm length and 50 mm diameter, carrying an extension with a hole at its closed end and a stout wire handle at the open end. The handle is equipped with a small metallic catch and a rope. The device is inverted in the position shown in Fig. 1.2, and lowered to the required depth in the oil. When the rope is jerked, the catch is released, whereupon the cylinder rights itself and fills with oil.

In Fig. 1.3 a sampling tube is shown. This consists of two concentric metal tubes closely fitted into each other throughout their length, so that one tube can be rotated within the other. Longitudinal openings are cut into each tube, so that in one position the tube is open and admits oil. When the inner tube is rotated the openings are closed and the tube becomes a sealed container. A further small rotation then opens some V-shaped parts at the lower ends of the tubes, so arranged to enable the instrument to be drained into a receiver while the longitudinal openings are still closed. Several other types of sampling device are described in the standards for sampling mentioned above. Large tanks of oil should be sampled at a number of depths in order to alleviate any variation in properties with depth, as it is not infrequent for oils to 'layer' within a tank especially if there is a temperature variation. In general the temperature at which the oil is held prior to sampling should be 5 to 15 °C above its clear point. Table 1.1 gives the recommended ranges of temperatures within which liquid fats and oils should be held when the sample is taken.

Solid fats are best melted and rendered completely homogeneous, e.g. by stirring, before any sample is taken. Sometimes this is not feasible, however, and in these cases a fat trier such as that shown in Fig. 1.4 is used. This is made of metal, with a C-shaped cross-section. It is pushed into the fat, rotated and withdrawn with a plug or core of the fat. Fat triers are also used for sampling emulsified fats, such as butter or margarine, according to BS 809 Section 4. Three cores are drawn by inserting the trier vertically through the block of fat at the centre of the upper face, and near two diagonally opposed corners and directed through the centre of the block. The analytical sample is then

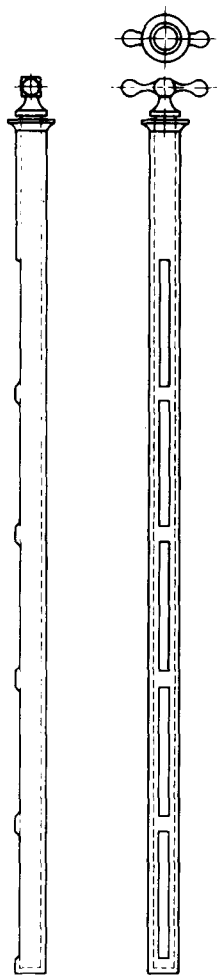


FIG. 1.3. Sampling tube. (Reproduced with permission of the BSI, London.)

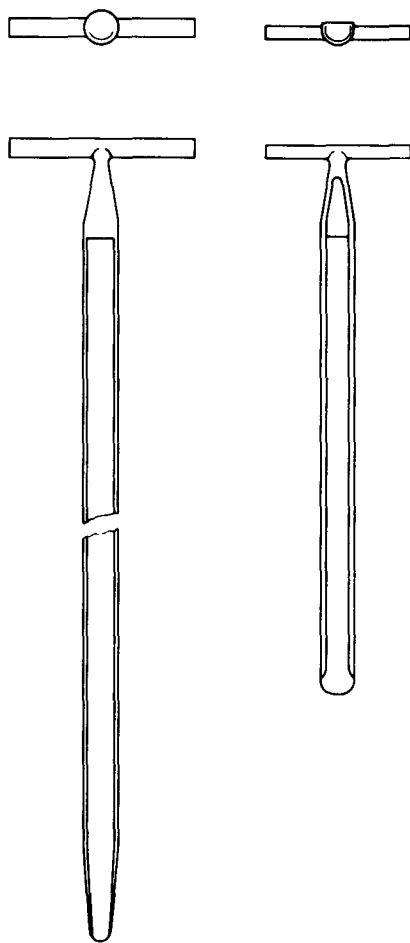


FIG. 1.4. Sampling triers. (Reproduced with permission of the BSI, London.)

prepared by taking the top third of the first core, the middle third of the second core, and the bottom third of the third core.

Analysis of the fat phase of an emulsified product necessitates separation of the fat from the emulsion. This should be carried out in such a way that the fat properties are not affected, e.g. excessive

TABLE 1.1
TEMPERATURE LIMITS FOR SAMPLING

<i>Product: source of fat or oil</i>	<i>Temperature, °C</i>	
	<i>min.</i>	<i>max.</i>
Olive, maize, rape, safflower, sesame, soya, sunflower, linseed.	15	25
Groundnut (arachis), tung	20	25
Cottonseed	20	30
Castor	25	35
Whale, fish oils	30	35
Sperm	35	40
Coconut	35	45
Palm kernel	40	45
Shea nut butter	45	50
Greases	45	55
Lard, palm oil	50	55
Tallow	50	60
Palm stearine	55	70

warming should be avoided if the peroxide value of the fat is in question. In general a sufficient quantity of the sample is melted at about 60 or 70 °C and kept warm until the bulk of the aqueous phase has settled out. The liquid fat is then decanted through a water-jacketed or warmed filter, as no partial solidification of the fat may be permitted during the filtration. Alternatively, the decanted fat may be centrifuged in warmed centrifuge tubes, to settle the finest droplets of aqueous phase. An alternative procedure is to pour the melted emulsion onto a column of anhydrous sodium sulphate and then wash the fat through the column with a solvent such as dry diethyl ether. The solution can then be filtered (if necessary) and the solvent removed under vacuum, thus avoiding oxidation of the fat. If a weighed amount of emulsion is added to the column, the yield of fat recovered from the solution is a reasonably reliable measure of the total fat content of the emulsion—this procedure being the basis of the IUPAC rapid method for the determination of total fat in margarine.¹

It will be seen that various metal devices are used for fat sampling, and care must be taken with regard to the construction of these. On no account should they influence the properties of the fat, and they are therefore best made of stainless steel. Copper, which is a powerful fat

oxidation catalyst, must not be used for any part of the sampling device.

Once the samples have been taken they should be properly packaged, labelled, and handled in such a way that there is no influence on any subsequent analysis. For example, where the subsequent analysis concerns the oxidative condition of the oil, as in the case of peroxide value, the sample should not be exposed to direct sunlight or overheated.

When wet or inhomogeneous samples are used, free water should be allowed to settle and its level measured to the nearest 2–3%; any suspended water is determined by weight loss of a portion of the supernatant oil by an approved method. The wet oil can be prepared for analysis by some suitable means such as decantation and filtration through a filter paper. Residual moisture may be removed by evaporation at 103 °C provided that the heating has no influence on the subsequent analytical tests. Samples which are turbid or contain a sediment, and which will not clarify on warming, should be filtered through a filter paper at a temperature about 10 °C above the melting point of the fat. The quantity and if possible the nature of the impurity should then be recorded along with the other results in the test report. Methods for the determination of insoluble impurities are given in BS 684, Section 2.3 (1983), ISO 663-1981, and IUPAC (ref. 2, method 2.604, p. 160), as described later.

Analytical methods used for manual or automatic process control can be manual (discontinuous) or in-line (continuous or discontinuous). The speed of the method (turn around time) and the frequency of sampling when discontinuous methods are used, must be related to the rate of variation of the true quality characteristics. This rate of variation depends on the characteristics of the process (time constants) and the disturbances acting on the process. At a given rate of variation of the uncontrolled process, the speed of the methods must be related to the time available for corrective action. The same applies to the sampling frequency when discontinuous methods are used. In these circumstances, for more effective process control it may well be necessary to sacrifice accuracy of the applied method for speed, as in many quality measurements accuracy and speed are conflicting requirements. Thus, selection of the most suitable method for process control demands close inspection of the characteristics of the process itself.

1.3 BASIC QUALITY CONTROL TESTS

The evaluation of a properly taken sample will, to a large extent, depend upon the state or condition of the fat, and its intended use.

Oils and fats are obtained from a variety of natural sources. Vegetable oils may be derived from oil-bearing seeds such as cottonseed, rapeseed, linseed, castor-bean, etc., or from nuts such as groundnut, coconut and shea nut. Palm and olive oils, however, come from the outer fleshy pulp of the fruit; in both cases the kernel also contains useful oil—palm kernel and olive kernel oils, respectively.

Animal fats may be obtained by rendering fatty parts of the animal carcass, or from mammalian milk, whilst fish oils are usually produced by crushing whole fish. In some cases, however, specific oils are obtained from selected organs, as with cod-liver oil. In the natural form many oils have a disagreeable colour, taste and odour. Such oils are termed 'crude' oils, and need refining if intended for edible use. A few oils called 'virgin oils' are prized in their natural condition, however, as they have a pleasant agreeable flavour, and are used in foods without further treatment. This is the case for instance with olive oil, cocoa butter, and dairy butter. Unless intended for industrial applications, crude oils must be refined before use and many of the basic quality control tests applied in the oil industry relate to the supervision of the industrial refining processes of bleaching, neutralisation and deodorisation.

Oils and fats have many varied applications, and although a specific oil type may be ideally suited for a certain food use, it can become highly priced. The interchangeability of oils has therefore become widespread, and oils which have inappropriate chemical or physical properties are modified, e.g. by hydrogenation, fractionation, inter-esterification or blending, to fit them for a specific purpose. Many tests are therefore carried out in order to control these various processes.

In this section it is therefore convenient to cover the basic quality control tests that may be applied to virgin, crude and refined oils, and to oils at intermediate stages of processing.

1.3.1 Taste

Many virgin oils will be graded primarily according to their taste, a necessarily subjective assessment. In some cases a flavour profiling technique may be applied in ranking oils or fats for use in foodstuff